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RESEARCH PAPER RP822

Part of Journal of Research of the National Bureau of Standards, Volume 15, September 1935

AN EXTENSOMETER COMPARATOR

By Ambrose H. Stang and Leroy R. Sweetman

ABSTRACT

An extensometer comparator for the calibration of extensometers, compressometers, micrometer dials, and strain gages is described. The comparator has given satisfactory results in calibrating length-measuring instruments used for materials testing.

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I. INTRODUCTION

In materials testing, loads and length changes are generally determined. Calibration of load-measuring devices can be accurately made using proving rings which are in turn calibrated by deadweights.[1] The need for a satisfactory apparatus for calibrating the length-measuring instruments used in materials testing has resulted in the design of the extensometer comparator shown in figure 1. Extensometers, compressometers, dial micrometers, and strain gages having a gage length of from ¼ to 24 in. can be calibrated on the comparator.

II. EXTENSOMETER COMPARATOR

1. GENERAL

The extensometer comparator shown in figure 1 consists essentially of a rigid frame, an adjustable crosshead, and the apparatus for length measurements.

2. FRAME

The main parts of the frame are the upper and lower yokes and the side tubes. The upper yoke a is a structural steel H-section; the lower yoke b is a portion of a structural steel H-section with 1

[1] L. B. Tuckerman, Herbert L. Whittemore, and Serge N. Petrenko, *A new deadweight testing machine of 100,000 pounds capacity*, BS J. Research **4**, 261 (1930) RP147.

flange cut off. The side tubes c are seamless drawn-steel tubing. The connections between these parts are made by the 4 solid-steel plugs d, bolted to the webs of the crossheads. One end of the plug is slotted, making a pressed fit over the web. The other end, a cylinder of smaller diameter, is a pressed fit with the machined inside surface of the tube end. The outside surfaces of the tubes were machined concentric with the inside surfaces. The tubes are parallel, permitting the adjustable crosshead e to be moved along the tubes without binding.

3. ADJUSTABLE CROSSHEAD

The sides of the adjustable crosshead are structural-steel channel sections with the flanges toward each other. The flange edges are machined to fit the tubes of the frame. The crosshead may be placed at the proper distance from the measuring end, according to the gage length of the instrument to be calibrated, and locked in position by tightening the handles f on the bolts holding the channels together.

4. SPINDLES

Both the measuring end and the adjustable crosshead are provided with spindles, coaxial with each other, to which the instrument may be fastened. If the instrument is a hand strain gage, the instrument points may be inserted in gage holes on a plane through the axis of the spindle. Fixtures for other types of length-measuring devices may be attached to the ends of the spindles by the type of coupling g shown in figure 2 at the end of movable spindle h.

Spindle i (fig. 1) in the adjustable crosshead is also adjustable with respect to the crosshead for a distance of about 6 in. and may be locked in position. This feature makes it unnecessary to move the entire crosshead for small changes in gage length. Accuracy in setting the relatively heavy crosshead for different gage lengths is therefore unnecessary.

5. MEASURING APPARATUS

A diagrammatic view of the measuring end of the comparator is shown in figure 2. The movable spindle in this end is moved relative to the fixed spindle in the adjustable crosshead by means of handwheel j threaded on the spindle and actuated by worm k attached to the frame. The worm may be disengaged for rapid movement of the spindle. The threaded portion of the spindle has 20 threads per inch, the circumference of the wheel 360 teeth. One turn of the worm causes a movement of the spindle of 0.00014 in. An angular motion of about 260° in the worm moves the spindle 1/10,000 in. Relatively sensitive adjustments may, therefore, be made. The movable spindle is prevented from rotating by torque arm l.

Compression spring m, located between the frame and auxiliary disk n threaded on the movable spindle and keyed by pins o to the handwheel, takes up backlash in the threads. This feature allows the comparator to be used in any position, horizontal, vertical, or inclined. The position of the movable spindle does not depend on gravity. A force of about 70 lb on the spindle produced by the spring is sufficient to prevent motion of the spindle due to forces set up by the mechanism of the instrument to be calibrated. Ball

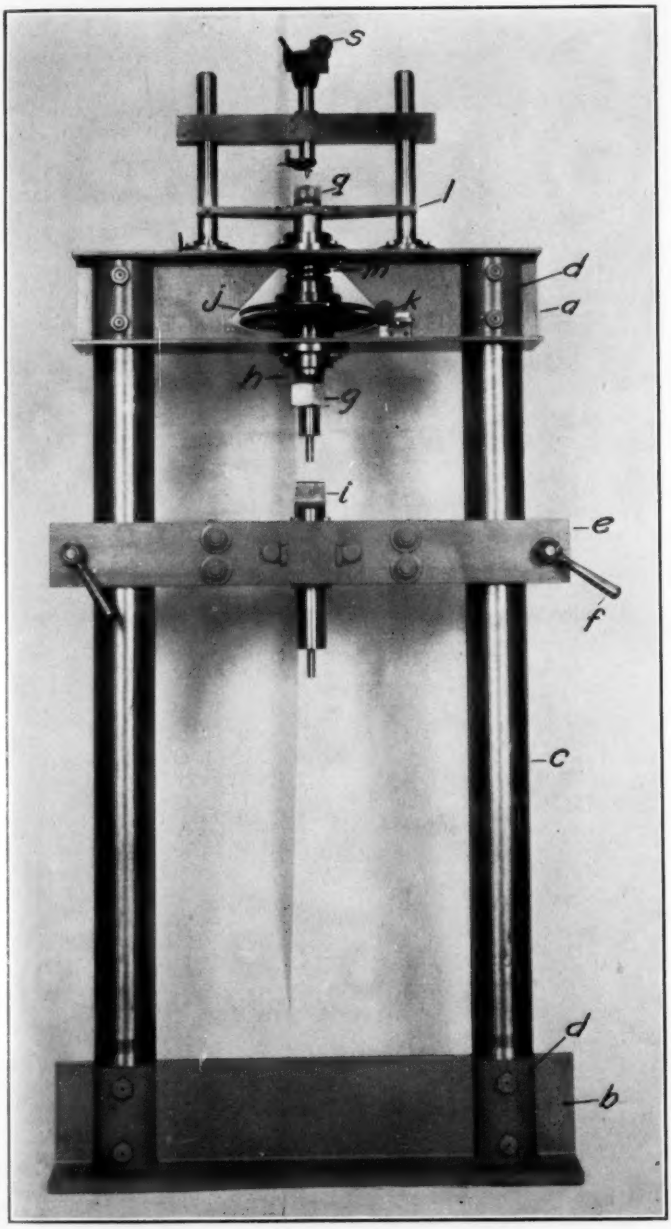

FIGURE 1.—*Extensometer comparator.*

thrust bearings p, located between the frame and the spring and between the frame and the handwheel, are provided with dust covers.

The upper end of the movable spindle is provided with vise q, in which a standard gage block r is clamped. Indicator s is attached

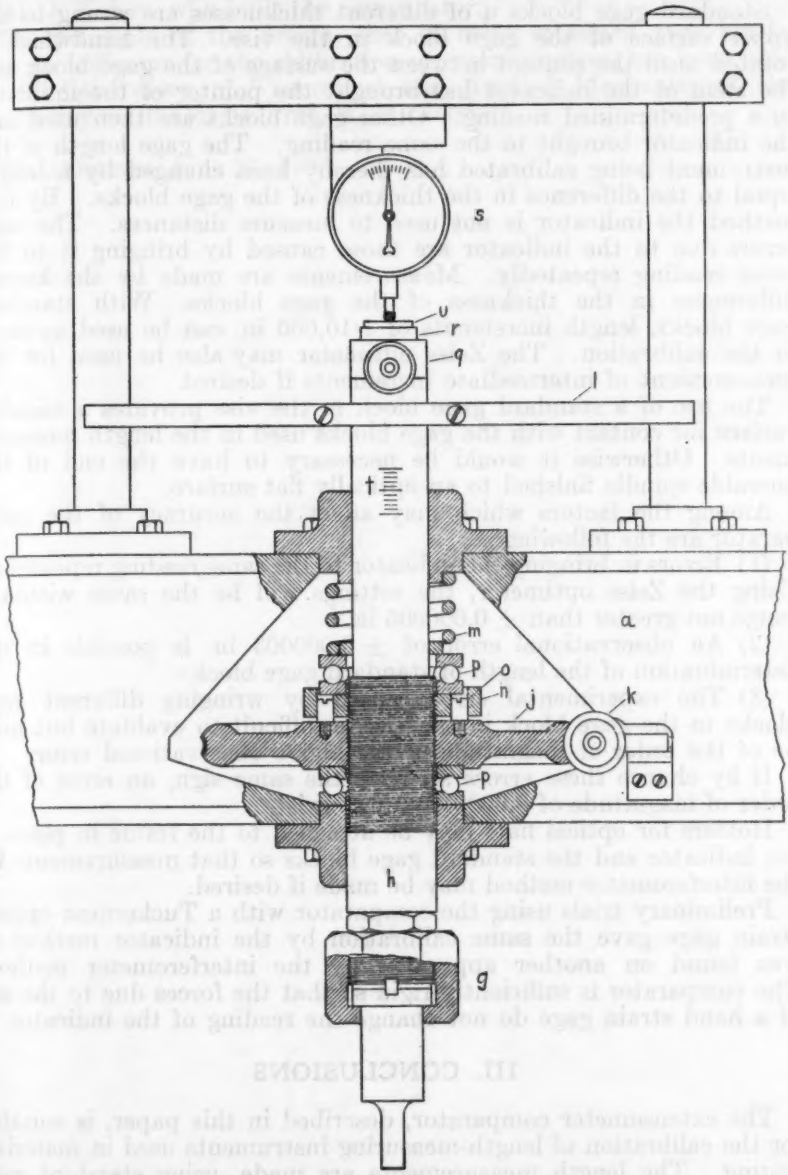

FIGURE 2.—*Measuring end of extensometer comparator.*

to the upper crosshead. The indicator shown in figure 1 is a Zeiss optimeter and in figure 2 a dial micrometer.

The range of the extensometer comparator is 1 in. Scale t, graduated in tenths of an inch, is on the surface of the movable spindle.

The reading of this scale indicates whether the movable spindle is or is not in the proper working position.

6. METHOD OF CALIBRATING AN INSTRUMENT

Standard gage blocks u of different thicknesses are wrung to the upper surface of the gage block in the vise. The handwheel is rotated until the contact between the surface of the gage block and the stem of the indicator has brought the pointer of the indicator to a predetermined reading. Other gage blocks are then used and the indicator brought to the same reading. The gage length of the instrument being calibrated has thereby been changed by a length equal to the difference in the thickness of the gage blocks. By this method the indicator is not used to measure distances. The only errors due to the indicator are those caused by bringing it to the same reading repeatedly. Measurements are made by the known differences in the thickness of the gage blocks. With standard gage blocks, length increments of 1/10,000 in. can be used as steps in the calibration. The Zeiss optimeter may also be used for the measurement of intermediate increments if desired.

The use of a standard gage block in the vise provides a suitable surface for contact with the gage blocks used in the length measurements. Otherwise it would be necessary to have the end of the movable spindle finished to an optically flat surface.

Among the factors which may affect the accuracy of the comparator are the following:

(1) Errors in bringing the indicator to the same reading repeatedly. Using the Zeiss optimeter, the settings will be the same within a range not greater than $\pm$ 0.000005 in.

(2) An observational error of $\pm$ 0.000003 in. is possible in the determination of the length of standard gage blocks.

(3) The experimental error caused by wringing different gage blocks to the gage block in the vise is difficult to evaluate but may be of the order of magnitude of the above observational error.

If by chance these errors all have the same sign, an error of the order of magnitude of 0.00001 in. may exist.

Holders for optical flats may be attached to the frame in place of the indicator and the standard gage blocks so that measurements by the interferometer method may be made if desired.

Preliminary trials using the comparator with a Tuckerman optical strain gage gave the same calibration by the indicator method as was found on another apparatus by the interferometer method. The comparator is sufficiently rigid so that the forces due to the use of a hand strain gage do not change the reading of the indicator.

III. CONCLUSIONS

The extensometer comparator, described in this paper, is suitable for the calibration of length-measuring instruments used in materials testing. The length measurements are made, using standard gage blocks of known thickness. The comparator may be used in any position. Forces exerted by the instrument being calibrated do not affect the accuracy of the calibration.

The extensometer comparator was designed by members of the Engineering Mechanics Section and built in the Bureau instrument shop. Valuable suggestions and assistance in the design were given by D. R. Miller, Chief, Gage Section; by members of his staff; and by H. J. Kaiser, who built the comparator.

The principle of the design, that of using standard gage blocks with an indicator for the calibration of extensometers, has been used in the Laboratory of Theoretical and Applied Mechanics at the University of Illinois by Prof. H. F. Moore.

WASHINGTON, June 29, 1935.

U. S. DEPARTMENT OF COMMERCE NATIONAL BUREAU OF STANDARDS

RESEARCH PAPER RP823

Part of Journal of Research of the National Bureau of Standards, Volume 15, September 1935

PURIFICATION OF GALLIUM BY FRACTIONAL CRYSTALLIZATION OF THE METAL [1]

By James I. Hoffman and Bourdon F. Scribner

ABSTRACT

It is shown in this paper that if gallium, containing (as impurities) small amounts of antimony, bismuth, chromium, cobalt, columbium, copper, gold, indium, iron, lead, manganese, mercury, molybdenum, nickel, osmium, palladium, platinum, rhodium, ruthenium, silver, thallium, tin, vanadium, and zinc, is subjected to fractional crystallization of the metal, all the impurities named tend to concentrate in the crystalline portion, with the following exceptions: Silver, mercury, indium, lead, and tin are concentrated in the molten residue; copper and thallium remain about equally divided between crystals and residue; zinc is dissolved by the hydrochloric acid under which the crystallization takes place, and is entirely eliminated.

It is also shown that separation from iron or platinum in excess of 0.001 percent, from indium or lead in excess of 0.01 percent, or from tin in excess of 0.02 percent by fractional crystallization of the metal is impracticable.

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I. INTRODUCTION

Fractional crystallization of the metal has been used in the purification of gallium by T. W. Richards and W. M. Craig [2] and by one of the authors.[3] Either by inference or by direct statement, the reader is led to believe that the crystals become purer and the residue less pure as recrystallization is continued. Thus, Richards and Craig state that they made use of the process of fractional crystallization of metallic gallium in order to eliminate any residual trace of other nonisomorphous metals, and in the work at this Bureau a similar process was used to eliminate the last traces of lead and indium. In both cases the crystals were found to be purer than the residue. In our recent work it was found, however, that platinum, iron, manganese, and certain other metals are collected in the crystals and practically eliminated from the uncrystallized portion. Consequently, it was deemed desirable to determine whether impurities, likely to be

[1] The work described was done in connection with the purification of about 300 g of gallium for researches by Frederick J. Bates of the polarimetry section at the National Bureau of Standards.

[2] J. Am. Chem. Soc. **45**, 1155 (1923).

[3] James I. Hoffman, J. Research NBS **13**, 665 (1934) RP734.

present in gallium, tend to go into the crystals or into the residue during the process of fractional crystallization.

The fact that the crystals, obtained in our previous work and in that of Richards and Craig, were purer than the residue, shows that preliminary purifications had completely eliminated those elements which tend to collect in the crystals.

II. PREPARATION AND CRYSTALLIZATION OF IMPURE GALLIUM

In order to secure gallium containing such impurities as might be obtained by electrolysis of an alkaline solution, a portion of very impure metal was first prepared by electrodeposition [4] from a 10-percent solution of sodium hydroxide to which had been added, usually as chlorides or sulphates, 10 g of pure gallium and 2 mg each of antimony, arsenic, bismuth, cadmium, cerium, chromium, cobalt, columbium, copper, germanium, gold, indium, iridium, iron, lead, manganese, mercury, molybdenum, nickel, osmium, palladium, platinum, rhenium, rhodium, ruthenium, silver, tantalum, thallium, tin, tungsten, uranium, and vanadium. Any precipitate which formed was allowed to float in the solution during the electrolysis, to permit contamination by as many of the added elements as possible. Spectrochemical tests showed that the deposited gallium contained antimony, bismuth, chromium, cobalt, columbium, copper, gold, indium, iron, lead, manganese, mercury, molybdenum, nickel, osmium, palladium, platinum, rhodium, ruthenium, silver, thallium, tin, and vanadium. Although there is no assurance that any of the elements was quantitatively deposited, this gallium was so impure that crystallization of the metal was difficult. Consequently, two other portions of metal were prepared by mixing weighed amounts of this impure metal with pure metal in such proportions that the quantities of the elements contaminating the gallium were in the ratio 100:10:1 in the 3 alloys.

Since none of these alloys contained iridium, rhenium, and zinc, a fourth 10-g portion was prepared by electrolysis under the conditions previously stated, excepting that the alkaline electrolyte in this case contained only gallium and 5 mg each of iridium and rhenium, and 10 mg of zinc. Spectrochemical tests showed that only zinc and a very faint trace of rhenium were deposited with the gallium. It was observed during this work that usually only faint traces of cobalt, columbium, and rhenium were deposited.

These four 10-g portions of impure gallium were subjected to fractional crystallization as described by one of the authors.[5] This process, as recommended for a 50–g portion of metal, is as follows:

> To the gallium in a 50-ml beaker, add sufficient distilled water to cover the metal to a depth of about 0.5 cm, warm to about 50° C, and then add 5 to 10 drops of hydrochloric acid. Set the beaker in ice water, and, when the crystals appear, pick them out of the molten metal with the aid of glass-tipped tweezers. Continue picking out the crystals until only a small globule (0.5 to 1.0 g) of metal remains. Combine and melt the crystals, and by the same process repeat the crystallization until crystals of the desired purity are obtained. Reserve the hydrochloric-acid solution and the small globules of uncrystallized metal for further purification. During the last crystallization, drop the

[4] The electrodes and current density were the same as were used in the preparation of pure gallium, J. Research NBS 13, 665 (1934) RP734.

[5] J. Research NBS 13, 669 (1934) RP734.

crystals into cold alcohol and wash two or three times with alcohol by decantation. Dry the crystals by drawing clean dry air over them or by placing them in a desiccator over sulphuric acid. Preserve the crystallized metal in a stoppered flask.

Each portion of the impure gallium was fractionally recrystallized 10 times, about 0.5 g being allowed to remain uncrystallized every time. In this manner approximately equal amounts of crystals and uncrystallized residue were obtained from each original 10-g portion. The two portions, one consisting of the crystals and the other of the combined residues, were then melted separately in each case. Samples of the original and of these two portions were taken for spectrochemical analysis. These analyses showed that the elements deposited with the gallium are divided into the following classes when the impure metal is subjected to fractional crystallization:

1. Those that definitely tend to collect in the crystalline portion. These are antimony, bismuth, chromium, cobalt, columbium, gold, iron, manganese, molybdenum, nickel, osmium, palladium, platinum, rhodium, ruthenium, and vanadium. Traces of calcium and magnesium are often introduced by contact with containers or through dust. If present, these two elements likewise tend to concentrate in the crystalline portion.
2. Those that definitely tend to go into the residue. These are silver, mercury, indium, lead, and tin.
3. Those that show little tendency to accumulate in either the crystals or the residue. These are copper, thallium, and zinc.

In the process used by us, the metal is crystallized under dilute hydrochloric acid. In 10 crystallizations, zinc is usually entirely dissolved by the acid so that it does not appear in the crystals or the residue. The amount of rhenium that it has been possible to deposit with the gallium has usually been so small that it is difficult to state definitely whether it would collect in the crystals or the residue.

The spectrochemical analyses were made by means of a stigmatic concave-grating spectrograph,[6] and the spectra were examined for the sensitive lines of the elements involved.

III. APPROXIMATE QUANTITIES OF IMPURITIES THAT CAN BE SEPARATED BY FRACTIONAL CRYSTALLIZATION OF THE METAL

Since it is easily possible to recrystalize 100 g of gallium 25 times in 1 working day, fractional crystallization of the metal, without preliminary chemical purification, might seem to be a very efficient process for eliminating some of the impurities from the crude metal. It was noticed early in the work, however, that the process is not successful unless the amounts of impurities are very small.

Preliminary work showed that 35 recrystallizations of a portion of gallium containing 5 percent of indium and 0.03 percent of lead did not suffice to free the crystals from either indium or lead. Ten crystallizations, however, were sufficient to collect in the crystals practically all of 0.0003 percent of iron and all of the platinum that was introduced through attack of the electrodes during the deposition of gallium from a 10-percent solution of sodium hydroxide. One de-

[6] Described by W. F. Meggers, C. C. Kiess, and F. J. Stimson, BS Sci. Pap. 18, 244 (1922) S446; and by W. F. Meggers and Kelvin Burns, BS Sci. Pap. 18, 191 (1922) S441.

termination by chemical means indicated that platinum, so introduced, was not in excess of 0.001 percent.

In order to obtain further information on the elimination of small quantities of the impurities most frequently found in crude gallium, a 15-g portion of the metal, to which was added 0.02 percent each of lead, tin, and indium, and 0.05 percent of zinc, was subjected to fractional crystallization. By means of 25 crystallizations the metal was separated into 2 equal parts, one consisting of crystals and the other of residue. Spectrochemical analysis of samples taken from these melted fractions showed that zinc was entirely eliminated from both the residue and the crystals, and all but a faint trace of tin was eliminated from the crystals. The amounts of indium and lead had decreased in the crystals, but the indications are that these would not have been eliminated, even if the number of recrystallizations had been doubled. The same number of crystallizations failed to eliminate all the indium and lead from a similar portion of gallium containing only 0.01 percent of each. In this case, however, the indium was reduced to a faint trace and the lead to such an extent that it seemed probable that it could have been eliminated if the number of recrystallizations had been doubled.

Judging by the results obtained, it can be said that it is impracticable to eliminate from the crystallized portion quantities of lead and indium in excess of 0.01 percent, or tin in excess of 0.02 percent by fractional crystallization of the metal. In the case of zinc, 0.05 percent can easily be eliminated, and the limit is probably somewhat higher. Traces of iron and platinum, but probably not much in excess of 0.001 percent in either case, can be eliminated by discarding the first portions of the crystals. Quantitative data on elements other than lead, indium, tin, zinc, iron, and platinum were not obtained, because those mentioned are the only metals that were found in the crude gallium examined by us.

IV. DISCUSSION OF RESULTS

Gallium crystallizes in the tetragonal system. Of the metals in the impure gallium that was subjected to fractional crystallization, indium, thallium, and tin are the only ones that crystallize in the tetragonal system.[7] The fact that so many of these elements are found in the crystallized portion cannot, therefore, be explained on the basis of isomorphism. The distribution of many of the other elements between the crystals and the residue could probably be explained by means of the constitutional diagrams if these were known. However, if the gallium is contaminated by an appreciable amount of metals of the platinum group, a slight scum may form on it. It is probable that this scum adheres to the crystals as they are removed from the molten metal, thus accounting for the presence of members of the platinum group in the crystallized portion.

The application of the information given above is not difficult. As a concrete example, consider a lot of metallic gallium which has been found by chemical or spectrochemical tests to contain less than 0.001 percent each of iron and platinum, less than 0.01 percent each of lead and indium, less than 0.02 percent of tin, and approximately 0.05 percent of zinc. In this instance, it would be practicable to

[7] Int. Crit. Tables 1, 103-5 (1926)

make 10 fractional crystallizations in such a manner that the final combined residues would constitute about nine-tenths of the total quantity taken. The platinum and the iron would probably be contained in the small crystalline portion, which would be set aside for purification by other means. The combined residues could then be subjected to the usual fractional crystallization, which would tend to eliminate the other impurities mentioned from the crystalline portion. It should be noted that purification by this process is practicable only if a considerable quantity (50 g or more) of gallium is available. It was also found that if dilute hydrochloric acid is allowed to react with a portion of impure gallium until about nine-tenths of the metal is dissolved, practically all the lead remains in the undissolved portion.

WASHINGTON, July 12, 1935.

U. S. Department of Commerce National Bureau of Standards

RESEARCH PAPER RP824

Part of Journal of Research of the National Bureau of Standards, Volume 15, September 1935

PRESENT STATUS OF THE ISOLATION AND IDENTIFICATION OF THE VOLATILE HYDROCARBONS IN A MIDCONTINENT PETROLEUM [1]

By Robert T. Leslie [2] and Joseph D. White [2]

ABSTRACT

The work to date of the American Petroleum Institute's Research Project 6 on the fraction of a midcontinent petroleum boiling normally between 55 and 180° C is summarized. In the fraction, 55 to 145°, estimates have been made of the percentage contents of the 22 hydrocarbons actually isolated, the 6 hydrocarbons detected and in process of separation, and the 19 hydrocarbons whose presence in significant amounts is suspected. These quantities have been represented graphically in relation to the curves showing the distribution with temperature of the volume and the refractive index of the distillate. The composition of the large volumes of material which distilled in narrow temperature ranges before and after the removal of certain hydrocarbons is discussed.

It is probable that the foregoing 47 hydrocarbons will account for practically all of the material in this fraction. On this assumption the relative amounts of paraffin, naphthene, and aromatic hydrocarbons in the fraction are estimated to stand in the ratio of 6:3:1.

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I. INTRODUCTION

The work carried on at the National Bureau of Standards by the American Petroleum Institute Research Project 6 on the chemical constitution of petroleum, has reached the stage where it is profitable to survey the results obtained to date on the naphtha fraction of a midcontinent petroleum.

The study of the composition of petroleum is important, aside from its purely scientific interest, because of the rapidly increasing use of

[1] Financial assistance has been received from the research fund of the American Petroleum Institute. This work is part of Project 6, The Separation, Identification, and Determination of the Constituents of Petroleum.

[2] Research Associate at the National Bureau of Standards representing the American Petroleum Institute.

petroleum as a source of chemical raw materials. The importance is increased by the desire of the petroleum industry for information by which its more familiar products, gasoline and lubricating oil, may be intelligently improved.

In the present work [3] the analysis has been made as rigorous as possible by isolating hydrocarbons of sufficient purity to identify them by comparison of their physical properties with those of known hydrocarbons [1.2] [4] It has also been possible to estimate the rela-

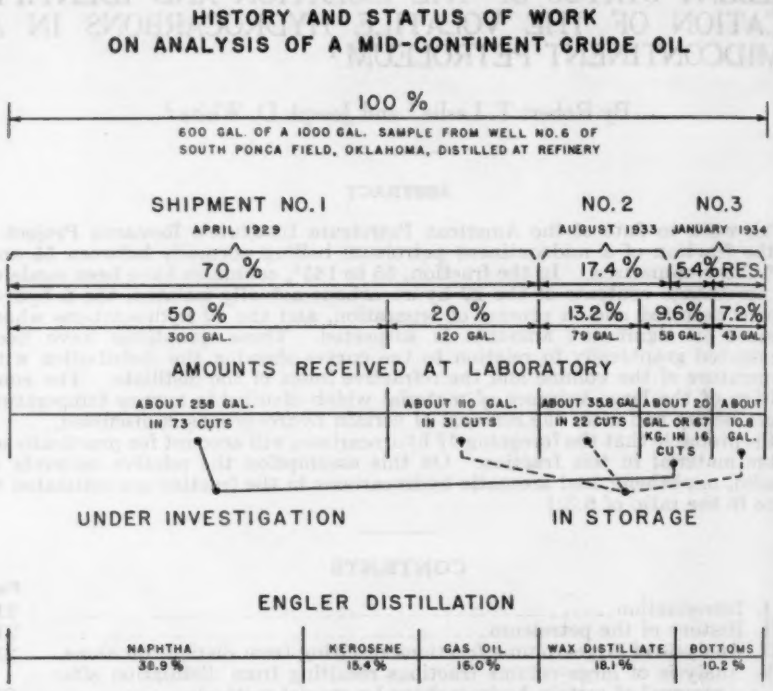

FIGURE 1.—*History and status of work on analysis of a midcontinent petroleum.*

Divisions showing percentages are drawn to scale on base line.

tive amounts of these hydrocarbons in the naphtha fraction as well as in the crude oil.

This paper surveys the results obtained so far on all the fractions of a midcontinent petroleum normally boiling between 55 and 145° C, and lists the constituents found in the fraction boiling between 145 and 180° C.

II. HISTORY OF THE PETROLEUM

In order to make the results of the work as complete as possible, a history of the petroleum from the well to the laboratory of the National Bureau of Standards has been kept. The essential details of volumes, percentages, and dates are shown graphically in figure 1. The original

[3] This investigation was begun in 1926 and was directed by E. W. Washburn until the time of his death in 1934. The work is being continued under the direction of F. D. Rossini. Individual contributions to the work have been reported at intervals in current scientific journals, and references to a number of these appear in this paper.

[4] Numbers in brackets refer to references at the end of paper.

3,800 liters (1,000 gallons) was supplied by the Marland Oil Co., from its well no. 6 in the South Ponca Field of Oklahoma, care being taken to avoid contamination with oils from other wells. It was shipped to the Sun Oil Co. for fractionation into quantities which could be handled in the laboratory. The assay distillation supplied by the Marland Oil Co. is shown at the bottom of the figure as an aid in identifying the laboratory fractions with their commercial classification. About 2,270 liters (600 gallons) of this material was carefully distilled in a small commercial still, and the lower-boiling fractions, representing about 70 percent of the crude oil, were sent to the laboratory in 1929 in approximately 12-liter fractions. The residue

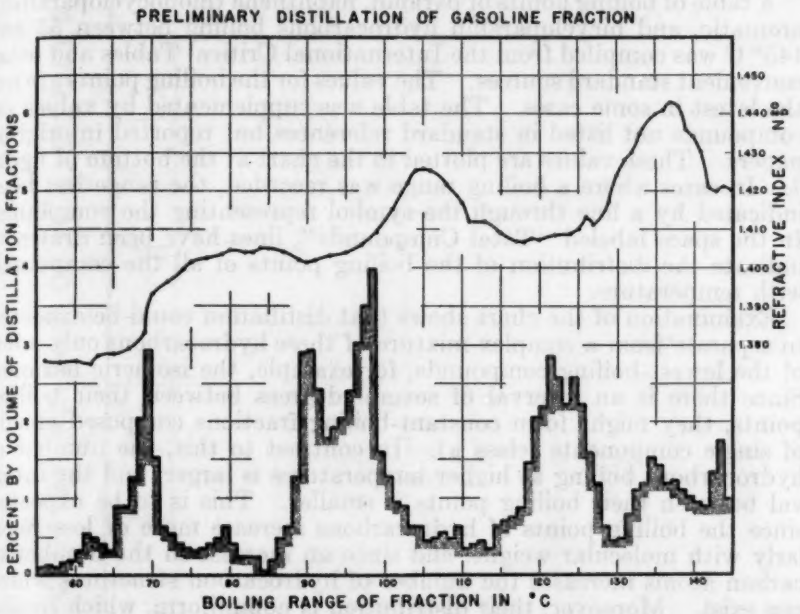

FIGURE 2.—*Preliminary distillation of the fraction of petroleum boiling between 55 and 145° C.*

The graph at the bottom of the figure shows the distribution of the volume with respect to boiling range. Volumes are indicated on the scale at the left. The curve at top of figure shows the refractive indices of distillation fractions boiling at 1 degree.

was divided into two approximately equal parts, one of which was carefully fractionated at reduced pressures and shipped to the laboratory at later dates.

Consecutive cuts of the lower-boiling fractions were redistilled in an atmosphere of carbon dioxide until the boiling point reached 240° C. The material redistilled represented approximately 50 percent of the original 2,270 liters. The distillate was carefully refractionated in laboratory stills [3] until considerable separation of material had occurred and further separation became slow.

Figure 2 shows the volumes and refractive indices of the fractions boiling between 55 and 145° C at the end of the preliminary distillation. Most of this graph was constructed from data appearing in previous papers [4, 5, 6, 7, 8, 9]. The remainder of the graph was con-

structed from data taken from unpublished notes. About 315 liters boiled within this region. Although this volume is about 14 percent of the 2,270 liters, it represents, by reason of losses, a considerably larger percentage of the crude oil. The distillate was distributed chiefly in 4 temperature ranges: 10 percent in the range 65 to 70° C, 30 percent in the range 90 to 100° C, 25 percent in the range 115 to 130° C, and 15 percent in the range 130 to 145° C.

III. ANALYSIS OF LARGE-VOLUME FRACTIONS RESULTING FROM DISTILLATION ALONE

A table of boiling points of paraffin, naphthene (monocycloparaffin), aromatic, and bicycloparaffin hydrocarbons boiling between 55 and 145° C was compiled from the International Critical Tables and other convenient standard sources. The values for the boiling points are not the latest in some cases. The table was supplemented by values for compounds not listed in standard references but reported in original papers. These values are plotted in the chart at the bottom of figure 3. In cases where a boiling range was recorded, the range has been indicated by a line through the symbol representing the compound. In the space labeled "Total Compounds", lines have been drawn to indicate the distribution of the boiling points of all the compounds with temperature.

Examination of the chart shows that distillation could be expected to separate from a complex mixture of these hydrocarbons only a few of the lowest-boiling compounds, for example, the isomeric hexanes. Since there is an interval of several degrees between their boiling points, they might form constant-boiling fractions composed chiefly of single components (class a). In contrast to this, the number of hydrocarbons boiling at higher temperatures is larger, and the interval between their boiling points is smaller. This is to be expected since the boiling points of hydrocarbons increase more or less regularly with molecular weight, and since an increase in the number of carbon atoms increases the number of hydrocarbon structures which can exist. Moreover, their distribution is nonuniform, which results in clusters of boiling points the complexity of which becomes greater with rising temperature. Distillation of a mixture of hydrocarbons boiling at the same temperature or in close proximity yields a fraction which is constant-boiling or substantially so. Such a fraction will be classed as that of the true solution type (class b). Constant-boiling fractions of this type can be separated completely only by the aid of other processes of fractionation in addition to distillation. The difficulty of separating a mixture by distillation alone is also complicated by the existence of a third class of constant-boiling fractions known as azeotropic mixtures (class c) which have minimum or maximum boiling point. These cannot be separated by simple distillation alone.

The analysis of petroleum may be less difficult than that of a mixture of all the possible hydrocarbons because it may contain fewer compounds in appreciable quantities; nevertheless it presents similar problems. It follows, therefore, that complete separation into component hydrocarbons of the large-volume fractions which result from the distillation of petroleum must be accomplished in stages in which certain of the hydrocarbons are removed by the application of special methods adapted to the particular fraction at hand. These large-

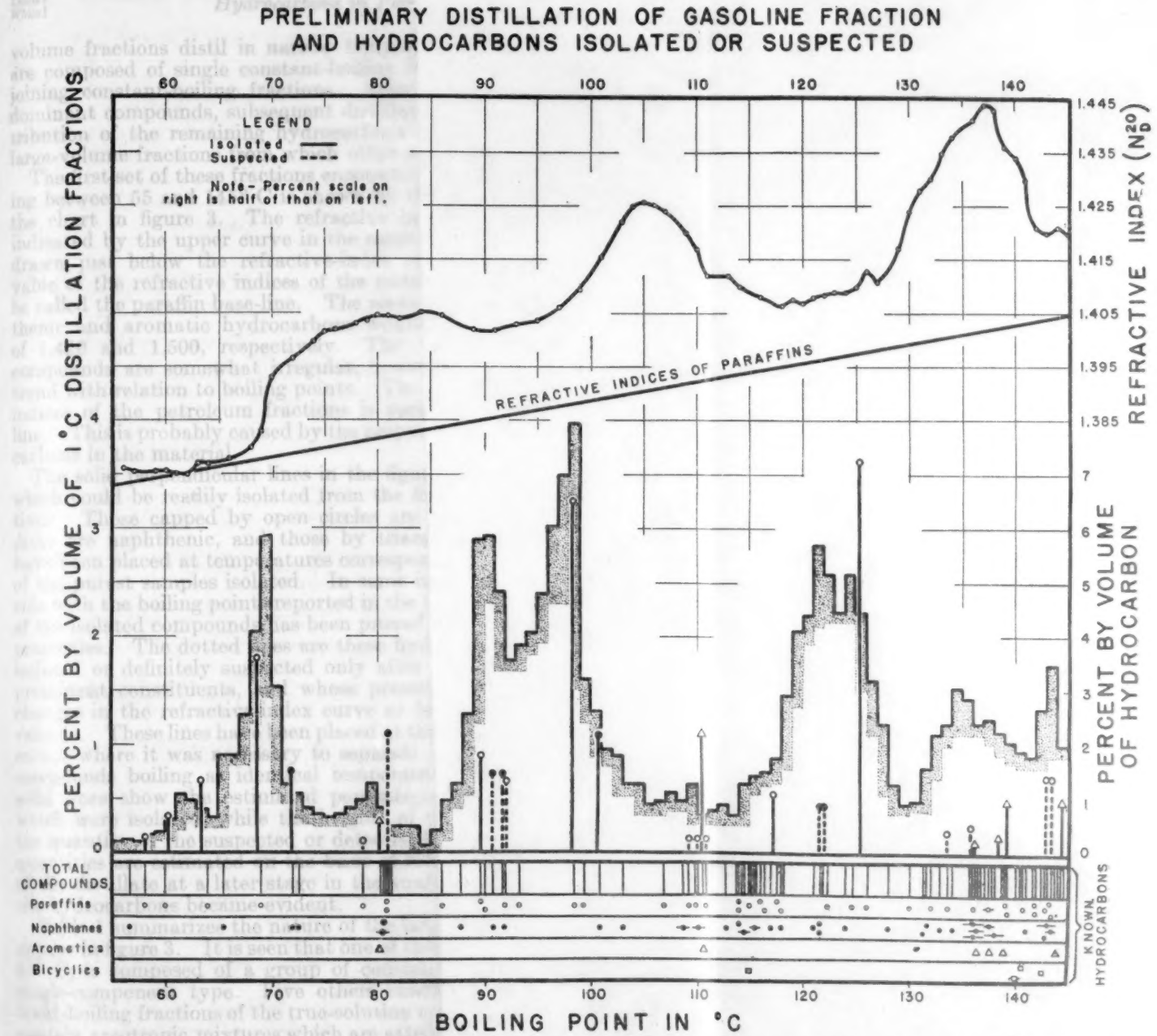

FIGURE 3.—*Composite graph of preliminary distillation, amounts of hydrocarbons removed or indicated, and distribution of boiling points of known hydrocarbons.*

The chart at the bottom of the figure gives the boiling points of known hydrocarbons, the different symbols representing the various classes. In the space entitled "Total Compounds", the lines show the distribution of all the boiling points.

Above the chart is shown the distillation graph with its volume scale to the left. The perpendicular lines, with their scale to the right, indicate the amounts of hydrocarbons isolated from or suspected in the distillate. (See legend in the figure.)

The curve at the top of the figure shows the refractive-indices of distillation fractions boiling at 1 degree intervals. The diagonal line below the refractive-index curve represents the mean values of the refractive indices of the paraffin hydrocarbons.

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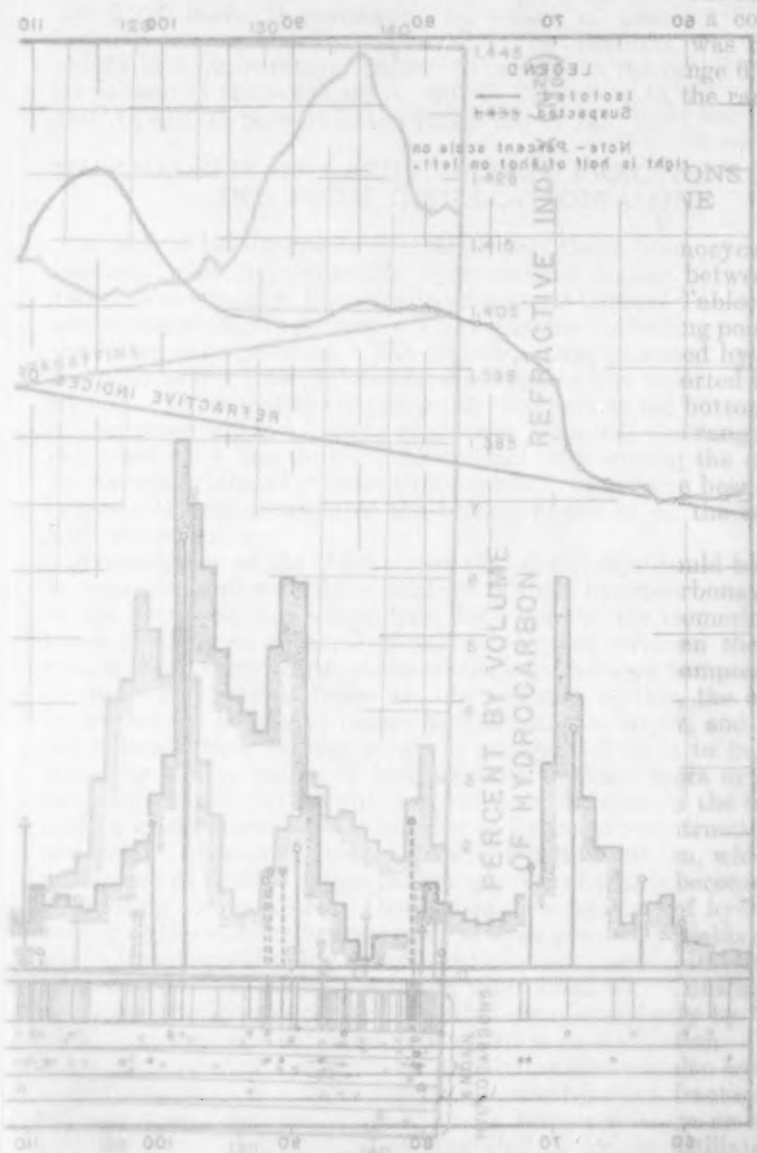
PERCENT BY VOLUME OF HYDROCARBON
REFRACTIVE INDEX
PERCENT BY VOLUME OF 1° C. DISTILLATION FRACTIONS

volume fractions distil in narrow temperature ranges because they are composed of single constant-boiling fractions or a group of adjoining constant-boiling fractions. After the isolation of the predominant compounds, subsequent distillations usually cause the distribution of the remaining hydrocarbons in a new set of relatively large-volume fractions from which other compounds can be isolated.

The first set of these fractions encountered in the petroleum distilling between 55 and 145° C is shown by the distillation curve above the chart in figure 3. The refractive indices of the fractions are indicated by the upper curve in the same figure. The diagonal line drawn just below the refractive-index curve represents the mean value of the refractive indices of the paraffin hydrocarbons and will be called the paraffin base-line. The mean refractive indices of naphthenic and aromatic hydrocarbons would lie in the neighborhood of 1.420 and 1.500, respectively. The values for the individual compounds are somewhat irregular, however, and show no definite trend with relation to boiling points. The tendency of the refractive indices of the petroleum fractions is parallel to the paraffin base-line. This is probably caused by the preponderance of paraffin hydrocarbons in the material.

The solid perpendicular lines in the figure represent hydrocarbons which could be readily isolated from the first set of distillation fractions. Those capped by open circles are paraffinic, those by solid disks are naphthenic, and those by triangles are aromatic. They have been placed at temperatures corresponding to the boiling points of the purest samples isolated. In some instances they fail to coincide with the boiling points reported in the literature, but the identity of the isolated compounds has been proved by the similarity of other properties. The dotted lines are those hydrocarbons which could be isolated or definitely suspected only after the removal of the more prominent constituents, and whose presence accounted in part for changes in the refractive-index curve or for slight accumulations of volume. These lines have been placed at their reported boiling points, except where it was necessary to separate slightly lines representing compounds boiling at identical temperatures. The heights of the solid lines show the estimated percentages of those hydrocarbons which were isolated, while the heights of the dotted lines represent the quantity of the suspected or detected hydrocarbons. The latter quantities are estimated on the basis of refractive index and volume of the distillate at a later stage in the analysis when the presence of the hydrocarbons became evident.

Table 1 summarizes the nature of the large-volume fractions which appear in figure 3. It is seen that one of these, boiling between 58 and 65° C, is composed of a group of constant-boiling fractions of the single-component type. Five others chiefly contain virtually constant-boiling fractions of the true-solution type. The remaining three contain azeotropic mixtures which are attributable to the presence of benzene, toluene, and the xylenes, respectively. The bulk of these aromatic constituents was found in those mixtures which boiled at considerably lower temperatures than the boiling points of the pure hydrocarbons [4, 10]. The abrupt rises in the refractive-index curve over the paraffin base-line correspond chiefly to the presence of aromatic compounds.

TABLE 1.—*Analysis of large-volume fractions of figure 3*

Approx. boiling range	Chief class of constant-boiling fraction present [1]	Nature of constituents	Names of chief constituents	Methods of separation or detection
°C				
58 to 65 [2]	a	Paraffinic	2,3-Dimethylbutane	Distillation.
			2-Methylpentane	Do.
			3-Methylpentane	Do.
65 to 71	c	Paraffinic	*n*-Hexane	Distillation with methyl and ethyl alcohol, nitration followed by crystallization.
		Naphthenic	Methylcyclopentane	
		Aromatic	Benzene	
76 to 81	b	Paraffinic	2,2-Dimethylpentane	Nitration followed by crystallization.
		Naphthenic	Cyclohexane	
		Aromatic	Benzene	
85 to 92	b	Paraffinic	2-Methylhexane	Crystallization with solvent.
			3-Methylhexane	Suspected from refractive-index curve.
		Naphthenic	1,2-Dimethylcyclopentane	
			1,3-Dimethylcyclopentane	
95 to 101	c	Paraffinic	*n*-Heptane	Nitration followed by distillation and crystallization.
		Naphthenic	Methylcyclohexane	
		Aromatic	Toluene	
107 to 110	b	Paraffinic	2,5-Dimethylhexane	Suspected from volume of distillate and refractive-index curve; toluene separated by nitration.
			2,4-Dimethylhexane	
			2,2,3-Trimethylpentane	
		Aromatic	Toluene	
115 to 127	b	Paraffinic	*n*-Octane	Crystallization with and without solvent.
			2-Methylheptane	
		Naphthenic	*m*-Dimethylcyclohexane	
			p-Dimethylcyclohexane	
131 to 140	c	Paraffinic	2,5-Dimethylheptane	Paraffins suspected from volume of distillate and refractive-index curve.
			2,4-Dimethylheptane	
		Aromatic	*o*-, *m*-, and *p*-Xylenes	Aromatics isolated by extraction and sulfonation.
			Ethylbenzene	
142 to 144	b	Paraffinic	2-Methyloctane	Paraffins suspected from refractive-index curve; aromatics isolated by extraction and distillation.
			3-Methyloctane	
		Aromatic	*o*-Xylene	

[1] a indicates a substantially pure substance; b, an ideal solution of 2 or more hydrocarbons having nearly identical boiling points; c, an azeotropic (minimum or maximum boiling) mixture.
[2] Resolved into 3 fractions by further distillation.

The hydrocarbons which have been separated from this first set of distillation fractions are as follows:

(1) The normal paraffins; hexane, heptane, octane.

(2) The 2-methyl derivatives of these normal paraffins.

(3) Two other isomers of hexane; 2,3-dimethylbutane and 3-methylpentane.

(4) Methylcyclopentane and methylcyclohexane.

(5) All the possible aromatic hydrocarbons; benzene, toluene, ethylbenzene and the three xylenes.

As indicated by their refractive indices, 6 of the distillation fractions contained hydrocarbons in addition to those isolated.

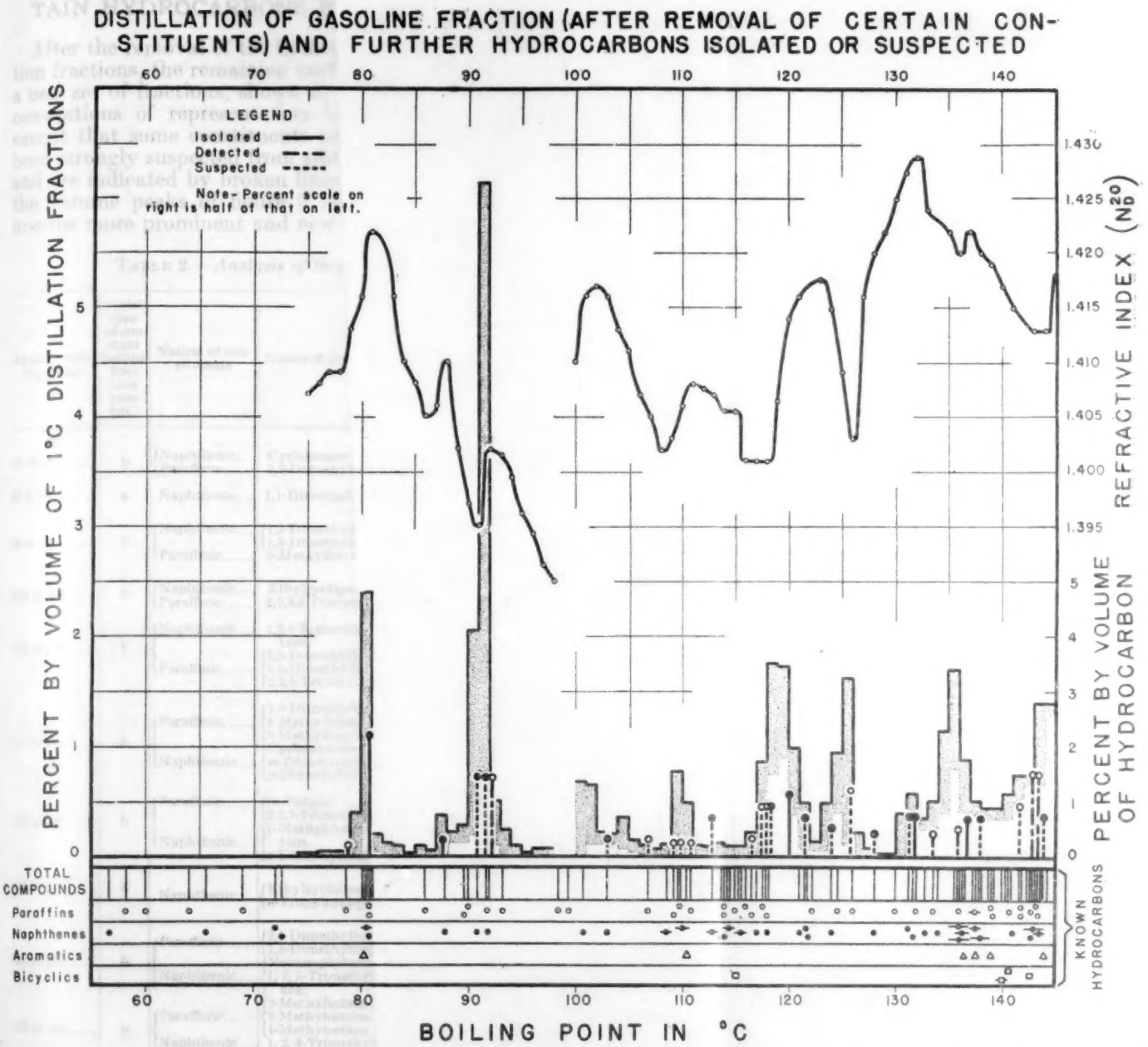

FIGURE 4.—*Composite of distillation after removal of certain constituents, amounts of hydrocarbons removed or indicated, and distribution of the boiling points of known hydrocarbons.*

[The representation of data is similar to that in figure 3.]

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LEGEND
Isolated
Detected
Evaporated
Note—Percent scale on right is not of that on left.
PERCENT BY VOLUME OF HYDROCARBON
REFRACTIVE INDEX
PERCENT BY VOLUME OF DISTILLATION FRACTIONS
TOTAL COMPOUNDS
Paraffins
Naphthenes
Aromatics
Olefins
60
70
80
90
100
BOILING POINT IN

IV. ANALYSIS OF LARGE-VOLUME FRACTIONS RESULTING FROM DISTILLATIONS AFTER REMOVAL OF CERTAIN HYDROCARBONS BY SPECIAL METHODS

After the removal of the hydrocarbons from the first set of distillation fractions, the remaining material was repeatedly redistilled until a new set of fractions, shown in figure 4, was obtained.[5] The same conventions of representation have been observed as in figure 3 except that some constituents not yet isolated, whose presence has been strongly suspected from additional data, are classed as detected and are indicated by broken lines. It will be observed that some of the volume peaks of figure 3 have disappeared while others have become more prominent and new ones have appeared. The changes

TABLE 2.—*Analysis of large-volume fractions of figure 4*

Approx. boiling range	Chief class of constant boiling fraction present [1]	Nature of constituents	Names of chief constituents	Method of separation or detection
°C				
79 to 81	b	Naphthenic	Cyclohexane	Crystallization.
		Paraffinic	2,2-Dimethylpentane	
87 to 89	a	Naphthenic	1,1-Dimethylcyclopentane	Do.
90 to 92	b	Naphthenic	1,2-Dimethylcyclopentane	Suspected from refractive index curve; 3-methylhexane detected by refractive index and chlorosulfonic acid treatment.
		Naphthenic	1,3-Dimethylcyclopentane	
		Paraffinic	3-Methylhexane	
103 to 106	b	Naphthenic	Ethylcyclopentane	Suspected from volume of distillate and refractive-index curve.
		Paraffinic	2,2,3,3-Tetramethylbutane	
109 to 111	b	Naphthenic	1,2,4-Trimethylcyclopentane	Do.
		Paraffinic	2,5-Dimethylhexane	
		Paraffinic	2,4-Dimethylhexane	
		Paraffinic	2,2,3-Trimethylpentane	
117 to 122	b	Paraffinic	3,4-Dimethylhexane	Crystallization with solvent or suspected from volume of distillate and refractive-index curve.
		Paraffinic	4-Methylheptane	
		Paraffinic	3-Methylheptane	
		Naphthenic	Cycloheptane	
		Naphthenic	*m*-Dimethylcyclohexane	
		Naphthenic	*p*-Dimethylcyclohexane	
123 to 127	b	Paraffinic	(*n*-Octane)	Suspected from volume of distillate and refractive index.
		Paraffinic	2,2,5-Trimethylhexane	
		Naphthenic	1-Methyl-2-ethylcyclopentane	
		Naphthenic	*o*-Dimethylcyclohexane	
130 to 132	b	Naphthenic	Ethylcyclohexane	Crystallization with solvent; the cyclopentane suspected from refractive index and behavior on freezing.
		Naphthenic	*n*-Propylcyclopentane	
134 to 137	b	Paraffinic	2,4-Dimethylheptane	Nonanaphthene isolated by crystallization; others detected after subsequent fractionation.
		Paraffinic	2,5-Dimethylheptane	
		Naphthenic	Nonanaphthene	
		Naphthenic	1, 3, 5-Trimethylcyclohexane.	
140 to 145	b	Paraffinic	2-Methyloctane	Detected from volume of distillate, refractive-index curve, and subsequent fractionation.
		Paraffinic	3-Methyloctane	
		Paraffinic	4-Methyloctane	
		Naphthenic	1, 2, 4-Trimethylcyclohexane.	

[1] a, indicates a substantially pure substance; b, an ideal solution of 2 or more hydrocarbons having nearly identical boiling points; c, an azeotropic (minimum or maximum boiling) mixture.

[5] Portions of this graph have been published in earlier papers [5, 6, 11, 12].

in slope in certain portions of the refractive-index curve have also become more marked because of the closer fractionation which could be obtained on the now less complex mixture. In the absence of aromatics these changes in refractive index become significant in predicting the presence of naphthenes and paraffins. The amounts of these predicted hydrocarbons were calculated by dividing the volume of the distillate boiling in a given temperature range between the naphthenes and paraffins in the ratio indicated by its refractive index.

Table 2 summarizes the results of a study of the large-volume fractions appearing in figure 4. Below 75° C the material has been completely identified and between 98 and 100° C all the material has been attributed to *n*-heptane and methylcyclohexane (7). Any other constituents in these boiling ranges were in such small quantities that their detection was considered impracticable. It will be observed that after the removal of the aromatic constituents, no pronounced tendency to form azeotropic mixtures was detected. All the large-volume fractions, except that at 87 to 89° C, have been explained by the presence of true solutions of hydrocarbons whose boiling points lie close together. This single exception was probably of the same type [6], in which other constituents were present in quantities too small to be detected.

V. STUDY OF THE COMPOSITION OF THE FRACTION BOILING BETWEEN 55 AND 145° C

Figure 5 is a chart of all the hydrocarbons obtained in the two stages of fractional distillation and special treatments to which the material was subjected. Tables 3, 4, and 5 list these hydrocarbons, with their estimated amounts, in their respective classes (paraffin, naphthene, and aromatic). An attempt has been made to estimate the quantities of the hydrocarbons present as percentages of the total volume, but the losses which have occurred prevent close estimates. The percentages can be compared among themselves, assuming that the content of each constituent has been estimated with the same degree of accuracy. When the entire fraction has been worked out, it will be possible to adjust the values of percentage content to represent more nearly the actual amounts. Meanwhile the figures are reported unadjusted so that they will remain consistent with the values of percentages already published. Table 3 shows that of the paraffin constituents, which account for about 33 percent of the total volume, the 3 normal ones form about 17 percent, 10 monomethyl derivatives 12 percent, 7 dimethyl derivatives 2.3 percent, and other types 1.7 percent. Similarly table 4 shows that 9 cyclopentanes form about 7.5 percent, 8 cyclohexanes 8.5 percent, and cyclopheptane 1.0 percent. Table 5 shows that benzene constitutes 0.6 percent, while its monomethyl derivative (toluene) amounts to 2.2 percent, and the ethyl and dimethyl derivatives to 2.5 percent.

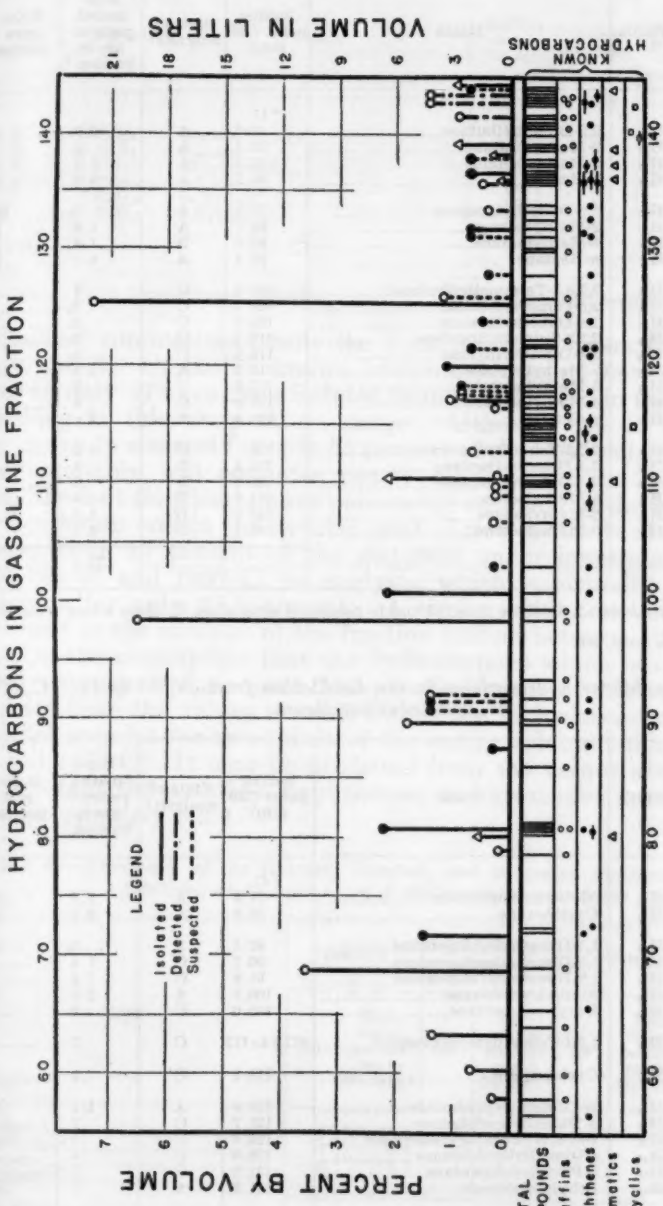

FIGURE 5.—*Composite graph of all the hydrocarbons isolated from or suspected in the fraction of petroleum boiling between 55 and 145° C after the two stages of distillation shown in figures 3 and 4.*

[The representation of data is similar to that in figures 3 and 4.]

TABLE 3.—*Paraffin hydrocarbons in the distillation fraction, 55 to 145° C, of a midcontinent petroleum*

No.	Formula	Name	Boiling point (760 mm)	State of analysis [1]	Estimated percentage in fraction [2]	Reference number
			°C			
1	C_6H_{14}	2,3-Dimethylbutane	58.0	A	0.3$_0$	[4, 13]
2	C_6H_{14}	2-Methylpentane	60.4	A	.6	[4, 13]
3	C_6H_{14}	3-Methylpentane	63.3	A	1.3	[4, 13]
4	C_6H_{14}	n-Hexane	68.7	A	3.6	[4, 13]
5	C_7H_{16}	2,2-Dimethylpentane	78.9	A	.2$_0$	[14]
6	C_7H_{16}	2-Methylhexane	89.7	A	1.8	[6]
7	C_7H_{16}	3-Methylhexane	92.0	B	1.4	
8	C_7H_{16}	n-Heptane	98.4	A	6.$_8$	[7]
9	C_8H_{18}	2,2,3,3-Tetramethylbutane	106.8	C	.3	
10	C_8H_{18}	2,5-Dimethylhexane	109.2	C	.2$_5$	
11	C_8H_{18}	2,4-Dimethylhexane	109.9	C	.2$_5$	
12	C_8H_{18}	2,2,3-Trimethylpentane	110.8	C	.2$_5$	
13	C_8H_{18}	3,4-Dimethylhexane	116.5	C	.3$_5$	
14	C_8H_{18}	2-Methylheptane	117.2	A	1.1	[15]
15	C_8H_{18}	3-Methylheptane	117.6	C	.9	
16	C_8H_{18}	4-Methylheptane	118.0	C	.9	
17	C_8H_{18}	n-Octane	125.4	A	7.$_3$	[8]
18	C_9H_{20}	2,2,5-Trimethylhexane	126	C	1.2	
19	C_9H_{20}	2,4-Dimethylheptane	133.5	B	.4	
20	C_9H_{20}	2,5-Dimethylheptane	135.9	B	.5	
21	C_9H_{20}	4-Methyloctane	141.6	B	.9	
22	C_9H_{20}	2-Methyloctane	142.8	B	1.5	
23	C_9H_{20}	3-Methyloctane	143.4	B	1.5	
Total					33.$_2$	

[1] A, those actually isolated; B, those detected and in process of separation; C, those whose presence is suspected.
[2] For significance see p. 218.

TABLE 4.—*Naphthene hydrocarbons in the distillation fraction, 55 to 145° C, of a midcontinent petroleum*

No.	Formula	Name	Boiling point (760 mm)	State of analysis [1]	Estimated percentage in fraction [2]	Reference number
			°C			
1	C_6H_{12}	Methylcyclopentane	71.8	A	1.5	[16]
2	C_6H_{12}	Cyclohexane	80.8	A	2.2	[5]
3	C_7H_{14}	1,1-Dimethylcyclopentane	87.5	A	.3$_0$	[6]
4	C_7H_{14}	1,3-Dimethylcyclopentane	90.7	C	1.4	
5	C_7H_{14}	1,2-Dimethylcyclopentane	91.8	C	1.4	
6	C_7H_{14}	Methylcyclohexane	100.8	A	2.2	[7]
7	C_7H_{14}	Ethylcyclopentane	103.0	C	.3	
8	C_8H_{16}	1,2,4-Trimethylcyclopentane	112.5 to 113	C	.7	
9	C_7H_{14}	Cycloheptane	118.1	C	.9	
10	C_8H_{16}	m-Dimethylcyclohexane	120.0	A	1.1	[11]
11	C_8H_{16}	p-Dimethylcyclohexane	121.7	C	.7	
12	C_8H_{16}	1-Methyl-2-ethylcyclopentane	124.0	C	.5	
13	C_8H_{16}	o-Dimethylcyclohexane	128.0	C	.4	
14	C_8H_{16}	n-Propylcyclopentane	131.3	C	.7	
15	C_8H_{16}	Ethylcyclohexane	131.9	A	.7	[17]
16	C_9H_{18}	Nonanaphthene (cyclopentane)	136.7	A	.7	[12]
17	C_9H_{18}	1,3,5-Trimethylcyclohexane	137 to 139	C	.7	
18	C_9H_{18}	1,2,4-Trimethylcyclohexane	143 to 144	C	.7	
Total					17.$_1$	

[1] A, those actually isolated; C, those whose presence is suspected.
[2] For significance see p. 218.

TABLE 5.—*Aromatic hydrocarbons in the distillation fraction, 55 to 145° C, of a midcontinent petroleum*

No.	Formula	Name	Boiling point (760 mm)	State of analysis [1]	Estimated percentage in fraction [2]	Reference numbers
			° C			
1	C_6H_6	Benzene	80.2	A	0.6	[4]
2	C_7H_8	Toluene	110.5	A	2.2	[10]
3	C_8H_{10}	Ethylbenzene	136.1	A	.2$_0$	[18]
4	C_8H_{10}	*p*-Xylene	138.4	A	.3$_0$	[9]
5	C_8H_{10}	*m*-Xylene	139.2	A	1.0	[9]
6	C_8H_{10}	*o*-Xylene	144.4	A	1.0	[9]
Total					5.3	

[1] A, those actually isolated.

[2] For significance, see p. 218.

Table 6 summarizes briefly the data shown in figure 5 and tables 3, 4, and 5. Of the 88 known compounds boiling between 55 and 145° C, only 47 have been isolated from or suspected in the petroleum distilling in this temperature range. Although the 47 compounds are shown to account for only 55 percent of the total volume, actually they probably will comprise nearly all the material. This arises from the fact that losses have necessarily occurred in the long process of distillation and in the development of new methods of separation. Thus, while 49 percent of the distillate under investigation boiled between 55 and 100° C, its analysis, which is virtually completed, accounts for only 25.5 percent. A similar situation will probably be found in the analysis of the fraction boiling between 100 and 145° C. On the assumption that the hydrocarbons which have been isolated or suspected account for practically all of the material, it appears from the values in table 6 that the 22 hydrocarbons already isolated account for two-thirds of the entire volume boiling between 55 and 145° C. It may be predicted from the values also given in table 6 that the paraffins, naphthenes, and aromatics are in the ratio of approximately 6:3:1.

TABLE 6.—*Summary of the isolated, detected, and suspected hydrocarbons in the fraction, 55 to 145° C, of a midcontinent petroleum*

Type	Isolated		Detected or suspected		Total		Known hydrocarbons reported boiling in the range 55 to 145° C
	No.	Estimated percentage in fraction [2]	No.	Estimated percentage in fraction [2]	No.	Estimated percentage in fraction [2]	
Paraffins	9	23.0	14	10.0	23	33.0	41
Naphthenes [1]	7	8.5	11	8.5	18	17.0	37
Aromatics	6	5.3			6	5.3	6
Bicycloparaffins							4
Total	22	37	25	18	47	55	88

[1] Monocycloparaffins.

[2] These values have been rounded to 2 figures. For significance, see p. 218.

VI. REPORT OF PROGRESS ON THE ANALYSIS OF THE PETROLEUM DISTILLATE BOILING BETWEEN 145 AND 180° C

Some work has been done on the fraction boiling between 145 and 180° C, but the ratio of the number of compounds isolated to the number known to boil in this range is smaller than that in the fraction boiling between 55 and 145° C. The information available concerning the 145 liters comprising this fraction will therefore be considered only briefly in this paper.

On distilling the material, a number of large-volume fractions resulted. Three of the more predominant ones boiled near 150, 160, and 170° C, respectively. The fraction boiling between 148 and 152° C contained 31 liters, a large portion of which was isolated as *n*-nonane [19]. The material boiling between 168 and 173° C (33.5 liters) contained *n*-decane [20] in amount nearly equal to that of *n*-nonane. Together these 2 normal paraffin hydrocarbons comprise about 28 percent of the total volume distilling between 145 and 180° C. From the material boiling near 160° C, mesitylene [21], and from the fraction, 168 to 173° C, pseudocumene and hemimellitene [21] have been isolated. Together they constitute another 4 percent of the total distillate. The presence of a number of other aromatic hydrocarbons is evident, especially the propylbenzenes and the ethyltoluenes in the material boiling between 150 and 160° C, and perhaps some of the butylbenzenes or methylpropylbenzenes in the material boiling from 170 to 180° C. It appears that a greater proportion of aromatic material will be found in the fraction 145 to 180° C, than in that boiling between 55 and 145° C. In addition to the normal paraffin and aromatic constituents the fraction contains isomeric decanes and napththenes.

Table 7 gives a summary of the constituents found so far in this fraction. All together, the 5 compounds listed are shown to comprise about 32 percent of the material boiling between 145 and 180° C. While this fraction no doubt contains other compounds, the complete analysis of the material will result in the isolation of a much smaller number of hydrocarbons than the 80 reported in the literature to boil within this region.

TABLE 7.—*Hydrocarbons isolated from the 145 to 180° C fraction of a midcontinent petroleum*

No.	Formula	Name	Boiling point (760 mm)	Estimated percentage in the fraction	Reference numbers
			°C		
1	C_9H_{20}	*n*-Nonane	150.7	15.5	[19]
2	$C_{10}H_{22}$	*n*-Decane	174.0	12.5	[20]
3	C_9H_{12}	Mesitylene (1, 3, 5-trimethylbenzene)	164.6	.3	[21]
4	C_9H_{12}	Pseudocumene (1, 2, 4-trimethylbenzene)	169.2	3.	[21]
5	C_9H_{12}	Hemimellitene (1, 2, 3-trimethylbenzene)	176.1	.9	[21]
Total				32.2	

TABLE 8.—*Hydrocarbons isolated*

No.	Formula	Hydrocarbon	Estimated amount in crude [1]	Purity of best sample [1,2]	Reference no.
			Percent	*Mole percent*	
		PARAFFINIC			
1	CH_4	Methane	a	a	
2	C_2H_6	Ethane	a	a	
3	C_3H_8	Propane	a	a	
4	C_4H_{10}	*n*-Butane	a	a	
5	C_5H_{12}	*n*-Pentane	a	a	
6	C_5H_{12}	2-Methylbutane	a	a	
7	C_6H_{14}	*n*-Hexane	0.5	98.3	[4]
8	C_6H_{14}	2, 3-Dimethylbutane		95	[13]
9	C_6H_{14}	2-Methylpentane	.3	95	[13]
10	C_6H_{14}	3-Methylpentane		95	[13]
11	C_7H_{16}	*n*-Heptane	.9	99.9	[7]
12	C_7H_{16}	2, 2-Dimethylpentane	.03	54	[14]
13	C_7H_{16}	2-Methylhexane	.25	99.9	[6]
14	C_7H_{16}	3-Methylhexane	b	b	
15	C_8H_{18}	*n*-Octane	1.0	99.1	[8]
16	C_8H_{18}	2-Methylheptane	.15	97	[15]
17	C_9H_{20}	*n*-Nonane	1.0	99.9	[19]
18	C_9H_{20}	2-Methyloctane	b	b	
19	C_9H_{20}	2, 5-Dimethylheptane	b	b	
20	$C_{10}H_{22}$	*n*-Decane	.8	99.9	[20]
		NAPHTHENIC			
21	C_5H_{10}	Cyclopentane	a	a	
22	C_6H_{12}	Methylcyclopentane	0.2	98.9	[16]
23	C_6H_{12}	Cyclohexane	.3	99.9	[5]
24	C_7H_{14}	Methylcyclohexane	.3	99.9	[7]
25	C_7H_{14}	1, 1-Dimethylcyclopentane	.04	95	[6]
26	C_8H_{16}	1, 3-Dimethylcyclohexane	.15	98	[11]
27	C_8H_{16}	Ethylcyclohexane	.1	95	[17]
28	C_9H_{30}	Nonanaphthene	.1	99	[12]
		AROMATIC			
29	C_6H_6	Benzene	0.08	99.8	[4]
30	C_7H_8	Toluene	.3	a	[10]
31	C_8H_{10}	*p*-Xylene	.04	99.9	[9]
32	C_8H_{10}	*o*-Xylene	.12	99	[9]
33	C_8H_{10}	*m*-Xylene	.12	99.9	[9]
34	C_8H_{10}	Ethylbenzene	.03	94	[18]
35	C_9H_{12}	Hemimellitene	.06	99.9	[21]
36	C_9H_{12}	Pseudocumene } trimethylbenzenes	.2	99.9	[21]
37	C_9H_{12}	Mesitylene	.02	99.9	[21]

[1] a, not determined; b, determination in progress.
[2] Values calculated from freezing-point data.

VII. CONCLUSION

At the stage of the work reported in this paper, somewhat more than half of the petroleum fraction distilling between 55 and 180° C has been separated into identified contituents. Of the remaining material boiling below 145° C, the greater part has been accounted for by other constituents, the presence of which is suspected from substantial evidence. Considered as a whole the analysis is less speculative and more complete than any similar work previously attempted. Such exact information concerning the individual constituents is not obtainable by the study of the distillation fractions alone but only by the actual isolation of identified compounds. All the hydrocarbons which have been isolated thus far from the petroleum, and upon which this report is based, are given in table 8, together with their estimated purity and percentage content in the crude oil.

In the course of separating the individual hydrocarbons it has been necessary to develop methods which may be utilized on a larger scale for the production of these chemical individuals from petroleum. The analysis has resulted in information which makes it possible to predict the occurrence in similar crude oils of individual hydrocarbons whose presence accounts for the properties of the commercial products of petroleum.

The problem of analyzing the naphtha fraction of petroleum appears at the outset to be one of extreme difficulty. Actually, as more effective methods for the separation are developed and fewer compounds remain to be isolated, the nature of the work becomes less tedious. However, much remains to be done and much additional information will be available when the final report is made.

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HEATS OF VAPORIZATION OF EIGHT GASOLINES

By Ralph S. Jessup

ABSTRACT

Measurements of the heats of vaporization at 40° C of 8 gasolines were made with an estimated accuracy of about 3 percent. The fuels investigated included 1 natural gasoline, 2 aviation gasolines, 1 straight run naphtha, 3 cracked naphthas, and 1 "safety fuel." The last named fuel is a hydrogenation product, which is apparently richer in hydrocarbons of the aromatic series than the other fuels. The results on all the fuels, except the safety fuel, can be represented within the accuracy of the measurements by a linear function of either specific gravity or average volatility.

The application of the results to the problem of ice formation in the carburetors of aviation engines due to cooling produced by evaporation of the fuel is briefly discussed. It is concluded that large differences in the rates of formation of ice with different fuels cannot be attributed to differences in the heats of vaporization, but must be largely due to differences in the completeness of vaporization of the fuels in the carburetor, resulting from differences in volatility of the fuels.

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I. INTRODUCTION

The work described in this paper was undertaken to obtain data on the heats of vaporization of fuels used in automobile and aircraft engines. Such data are of importance in the analysis of engine performance, and also in connection with the problem of ice formation in the carburetor, resulting from the cooling produced by evaporation of the fuel.[1] Most previous measurements of the heats of vaporization of petroleum products have been made at relatively high temperatures, and values obtained by extrapolating the results of various observers to lower temperatures are not in satisfactory agreement.

II. APPARATUS AND METHOD

The method used consisted essentially in vaporizing a known mass of the fuel in a stream of air flowing through a coil of tubing immersed in the water of a calorimeter, and measuring the resulting change in temperature of the calorimeter. The heat of vaporization is then given by

$$L=\frac{C\Delta\theta}{m} \qquad (1)$$

[1] Allen, Rodgers, and Brooks, Soc. Automotive Engrs. J. 35, 417 (1934).

where C is the heat capacity of the calorimeter, $\Delta\theta$ is the temperature change of the calorimeter corrected for heat transfer between the calorimeter and its surroundings, and m is the mass of fuel evaporated.

The apparatus is shown schematically in figure 1. The vaporizing coil V is made of copper tubing $\frac{7}{16}$ inch in outside diameter and 12

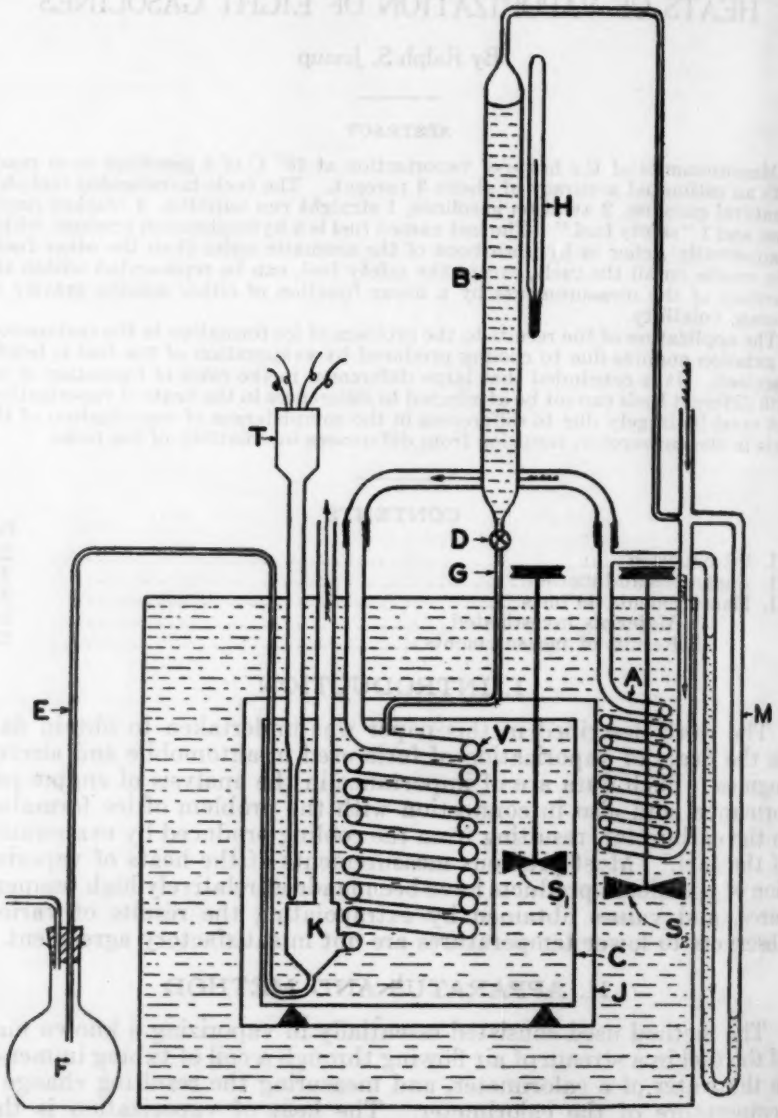

FIGURE 1.—*Schematic diagram of apparatus.*

feet long. It was immersed in the water contained in the calorimeter vessel C, which was completely inclosed by the jacket J. The jacket and calorimeter were separated at all points by a 1-cm air space.

The temperature of the jacket was kept constant within about 0.01° C by means of a thermo-regulator. The temperature of the

calorimeter was measured by means of the platinum resistance thermometer T. The screw propellors S_1 and S_2 were used to stir the water in calorimeter and jacket, respectively. The calorimeter and jacket have been described previously.[2]

A stream of air flowed first through the coil of copper tubing A immersed in the jacket water, and then through a rubber tube to the vaporizing coil V. The manometer M was used to indicate the rate of flow of the air.

The fuel to be vaporized was contained in the 25 ml burette B, and flowed to the vaporizing coil V through a small copper tube which was soldered to the jacket wall for a distance of about 17 inches.

The heat capacity of the calorimetric system was calculated from the masses and specific heats of the water and metal parts (mostly copper). The value used for the specific heat of water at 40° C is 4.173 international joules per gram degree C.[3] The calculated heat capacity of the calorimeter was 13,950 international joules per degree C. This value was checked experimentally by measurements of the heat of vaporization of water, the results of which are summarized in table 1.

The procedure in making a measurement of heat of vaporization of a fuel was as follows: The temperature of the calorimeter was adjusted to approximate equality with that of the jacket, and the flow of air through the vaporizing coil was started. The burette B (fig. 1) was filled with the fuel, and enough of this fuel was allowed to flow into the tube G to fill it completely, after which the valve D was closed. After sufficient time had elapsed for the establishment of a steady state, the position of the liquid meniscus in B, and the temperature indicated by the mercurial thermometer H were observed. From this time to the end of the experiment a reading of the temperature of the calorimeter was made each minute. After about 10 minutes of such observations the valve D was opened, allowing the fuel to flow to the vaporizer. When the liquid meniscus in the burette reached the lowest graduation the valve D was again closed. Any unevaporated residue which reached the chamber K was from time to time drawn through the tube E into the flask F and, after the completion of the experiment, was weighed. The observations of the temperature of the calorimeter were continued from 10 to 20 minutes after the time-temperature curve indicated that no more fuel was being evaporated. The mass of the fuel evaporated was calculated from the volume of fuel delivered to the vaporizer as measured by means of the burette, the density of the fuel, and the mass of the unevaporated residue.

The correction for heat transfer between the calorimeter and its surroundings was calculated from the observed rates of change of the temperature of the calorimeter at the beginning and end of the experiment when air was flowing through the vaporizing coil but no fuel was being evaporated. In making this calculation it was assumed that the rate of transfer of heat was a linear function of the calorimeter temperature. The heat transfer calculated in this way includes the heat transfer between the calorimeter and the stream of air flowing through the vaporizing coil.

[1] Bul. BS 11, 189 (1914) S230. J. Research NBS 13, 469 (1934) RP721.
[2] Int. Crit. Tables 5, 113.

A correction was applied to the results to take account of the fact that the fuel entered the calorimeter at a temperature different from; that of the calorimeter. This correction was calculated using specific heat data given at Cragoe,[4] and assuming that the fuel entered the calorimeter at the temperature of the jacket and was cooled to the average of the initial and final temperatures of the calorimeter.

The total temperature change of the calorimeter in the measurements of heats of vaporization of gasolines ranged from 0.4 to 1.0° C. The corrected temperature change ranged from about 50 percent of the total for the least volatile fuel to about 95 percent of the total for the most volatile fuel. The time during which evaporation of a fuel was taking place varied from 10 to 100 minutes.

As a test of the accuracy attainable with the apparatus, measurements were made of the heats of vaporization of water and of benzene. The water used in these experiments was ordinary distilled water, and the benzene was of "reagent" grade obtained commercially, and was not further purified. The results on water are compared in table 1 with data reported by Osborne, Stimson, and Fiock,[5] and the results on benzene are compared in table 2 with data reported by Fiock, Ginnings, and Holton.[6] In the present measurements the rate of flow of liquid to the vaporizing coil was varied over a considerable range in order to determine whether the results were affected by such variation.

TABLE 1.—*Comparison of data on water with data reported by Osborne, Stimson, and Fiock*

Experiment	Mean temperature	Percentage evaporated in present work	Heat of vaporization		Difference
			Present work	Osborne, Stimson, and Fiock	
	°C		int. j/g	int. j/g	*Percent*
1	38.8	56	2,413	2,406	+0.2
2	38.1	86	2,416	2,409	+.3
3	38.0	96	2,420	2,410	+.4

TABLE 2.—*Comparison of data on benzene with data reported by Fiock, Ginnings, and Holton*

Experiment	Mean temperature	Rate of vaporization in present work	Heat of vaporization		Difference
			Present work	Fiock, Ginnings, and Holton	
	°C	g/min	int. j/g	int. j/g	*Percent*
1	39.7	0.5	428.2	422.3	+1.4
2	39.6	.9	425.8	422.4	+.8
3	39.7	1.1	424.8	422.3	+.6
4	40.4	1.6	424.8	421.9	+.6
5	39.6	2.1	424.7	422.4	+.6
6	40.0	.6	417.8	422.1	−1.0
7	39.8	.5	421.5	422.1	−.1

[4] Misc. Pub. BS 97 (1929).
[5] BS J. Research 5, 411 (1930) RP209,
[6] BS J. Research 6, 881 (1931) RP312.

Evaporation was not complete in any of the experiments on water, and a different percentage of the water was evaporated for each rate of flow. The benzene, on the other hand, was completely evaporated in every experiment, the different rates of flow resulting merely in different rates of evaporation. It is seen from tables 1 and 2 that, within the precision of the measurements, there is no systematic variation of observed heat of vaporization with percentage of liquid evaporated or with rate of flow of liquid to the vaporizer. The results obtained on water are higher than those reported by Osborne, Stimson, and Fiock by 0.3 percent on the average, while the results on benzene are higher than those reported by Fiock, Ginnings, and Holton by 0.4 percent.

III. MEASUREMENTS ON FUELS

1. MATERIALS INVESTIGATED

The fuels on which measurements were made are listed in table 3, in which are also given for each material the source if known, ASTM distillation data, specific gravity, index of refraction, and average volatility. Average volatility is defined as the average of the three temperatures at which 10, 50, and 90 percent of the fuel was evaporated in the ASTM distillation test (percentage evaporated = percentage distilled, plus evaporation loss). The range of volatilities of the samples is somewhat wider than that of marketed gasolines. This fact was expected to result in a more definite indication of any variation of heat of vaporization with volatility.

TABLE 3.—*Description of samples*

Sample	Material	Source	Cracking process	ASTM distillation data— Initial	10%	30%	50%	70%	90%	End point	Loss	Residue	Average volatility	Specific gravity $60°/60°$ F.	Index refraction at 25.1° C n_D
				°C	°C	°C	°C	°C	°C	°C	%	%	°C		
1	Natural gasoline	Oklahoma		36	45	52	61	78	104	147	1.0	0.9	69	0.675	1.377_8
2	Aviation gasoline	do		55	65	70.5	76.5	84	98.5	115	1.4	.6	79	.696	1.386_6
3	do			44	67	78	87	95	108	143	1.0	.8	86	.729	1.404_1
4	Straight-run naphtha.	Los Angeles basin.		60	98	122	141	161	194	222	.7	1.2	143	.773	1.426_3
5	Cracked naphtha, 100%.	do	Cross	60	107	142	169	193	212	224	.6	1.1	162	.789	1.437_1
6	do			46	78	110	132	155	184	205	1.1	.9	130	.748	1.414_3
7	do	Oklahoma	Doherty	49	83	122	152	176	205	228	.7	1.3	145	.760	1.424_2
8	Safety fuel			156	165	170.5	175.5	181.5	191.5	205	.2	1.1	177	.874	1.492_4

The safety fuel (sample 8) is a hydrogenation product and differs considerably in some of its properties from the other fuels investigated. The heat of vaporization (fig. 2 and 3), heat of combustion,[7] and refractive index (table 3) of this fuel all indicate that it is richer in aromatic hydrocarbons than the other fuels listed in table 3. Aromatic constituents were also indicated by the following chemical tests. A sample of the fuel was examined for unsaturated hydrocarbons (olefins) by warming it with a solution of iodine in carbon

[7] Measured in this laboratory and found to be 10,400 calories per gram, as compared with values ranging from 10,000 to 10,500 calories per gram for the liquid aromatic hydrocarbons (Int. Crit. Tables 5, 162).

tetrachloride. The color of the iodine solution did not fade, indicating the absence of unsaturated constituents. A sample of the fuel was then treated with a mixture of fuming nitric and sulphuric acids in a vessel which was kept cool by running tap water over the outside. The fuel was almost entirely converted into nitro derivatives which, when poured on ice, partially froze to a yellow solid. This behavior is characteristic of aromatic compounds, and it appears probable that the fuel is composed largely of aromatic constituents. Copious evolution of brown NO_2 fumes during the nitration indicated that a portion of the fuel was oxidized rather than nitrated, and this portion may have been nonaromatic material.

2. RESULTS OF MEASUREMENTS

The results of the measurements on the various fuels are given in table 4. In none of the individual experiments did the average temperature of the calorimeter differ from 40° C (104° F) by more than 0.8° C, and in no case did the average temperature in all the experiments on any one fuel differ from 40° C by more than 0.3° C. Since the heats of vaporization of these materials change by only about 0.1 or 0.2 percent per degree C, the average values given in table 4 may, within the limits of experimental error, be taken as the heats of vaporization of the fuels at 40° C.

TABLE 4.—*Results of measurements*

SAMPLE 1

Experiment	Rate of flow of liquid to vaporizer	Percentage evaporated	Heat of vaporization	Percentage deviation from mean
	g/min		int. j/g	
1	0.8	100	350	0.0
2	1.1	100	351	+.3
3	2.2	100	354	+1.1
4	.6	100	346	−1.1
Mean			350	±.6

SAMPLE 2

1	0.9	100	349	−0.3
2	1.1	100	351	+.3
3	1.4	100	350	0
Mean			350	±.2

SAMPLE 3

1	1.3	100	352	0.0
2	1.0	100	353	+.3
3	1.9	100	351	−.3
Mean			352	±.2

SAMPLE 4

1	0.2	100	340	+0.9
2	.4	100	338	+.3
3	.3	99	325	−3.7
4	.9	85	344	+2.0
Mean			337	±1.7

SAMPLE 5

Experiment	Rate of flow of liquid to vaporizer	Percentage evaporated	Heat of vaporization	Percentage deviation from mean
	g/min		int. j/g	
1	0.75	66	326	+2.8
2	.7	65	311	−1.9
3	.15	95	310	−2.2
4	.4	77	321	+1.3
Mean			317	±2.0

SAMPLE 6

1	0.6	100	324	−0.6
2	.8	99	320	−1.8
3	.4	99.8	334	+2.5
Mean			326	±1.6

SAMPLE 7

1	0.5	87	316	−4.7
2	.2	99.5	323	−2.6
3	.35	93	333	+.5
4	1.1	65	348	+5.0
5	.4	87	334	+.8
6	.4	86	335	+1.1
Mean			331.8	±2.4

SAMPLE 8

1	0.2	98	370	−0.8
2	.9	45	382	+2.4
3	.25	92	380	+1.9
4	.5	68	365	−2.1
5	1.2	37.5	378	+1.3
6	.6	63	362	−3.0
7	.35	78	376	+.8
Mean			373	±1.8

There are two possible systematic errors in the results obtained from experiments in which the fuel was only partially evaporated. One of these errors results from the fact that the evaporated portion is richer than the original fuel in the more volatile constituents. The other error may arise from the failure of a small amount of the unevaporated residue to drain out of the chamber K (fig. 1), resulting in an error in the value used for the mass of fuel evaporated. These two errors are of opposite sign, and the fact that the data of table 4 do not show any systematic variation of observed heat of vaporization with percentage of fuel evaporated indicates that their combined effect is negligible in comparison with the accidental errors.

It is seen from table 4 that fair precision was attained in the measurements on samples 1, 2, and 3, which were sufficiently volatile so that they could be completely vaporized in relatively short times.

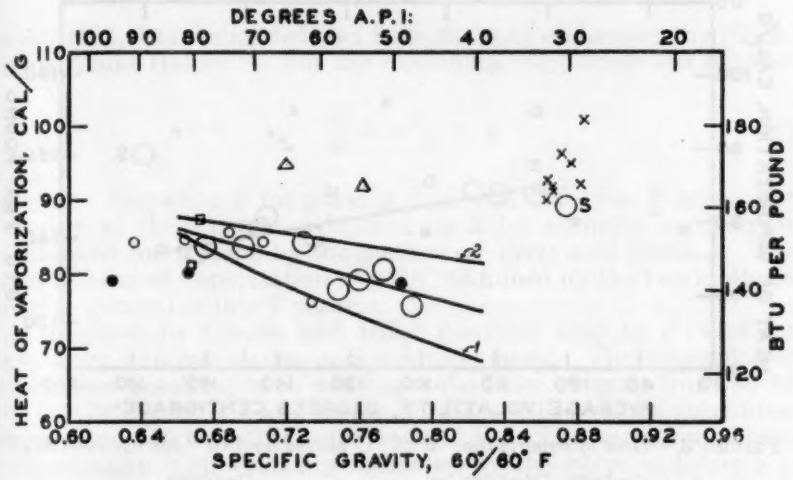

FIGURE 2.—*Heat of vaporization at 40° C plotted against specific gravity.*

○=Fuels. ○S=Safety fuel.
○=Normal paraffins.
●=Isoparaffins.
□=Olefins.
△=Naphthenes.
×=Aromatics.

For the remaining samples, which were considerably less volatile, the precision was not so high, the average deviation from the means being of the order of 2 percent and the maximum deviation 5 percent.

Lower precision in the measurements on the less volatile fuels is to be expected because, for a fuel of low volatility, the time required to vaporize a large fraction of the sample was so long that the change in temperature of the calorimeter due to heat interchange with its surroundings was of the same order of magnitude as the change in temperature produced by evaporation of the fuel. Consequently, the error in the value obtained for the heat of vaporization of the fuel resulting from error in the correction for heat transfer was of the same order of magnitude as the error in this correction. The error in this correction was greater in the present measurements than in many calorimetric experiments, because a large part of the heat transfer was between the calorimeter and the stream of air flowing through the vaporizer, and this heat transfer was affected by changes in room temperature and changes in the rate of flow of air, neither

of which was entirely constant. Decreasing the correction for heat transfer by shortening the time of the experiment resulted in a smaller fraction of the sample being evaporated, with a consequent reduction in the temperature change of the calorimeter, and in the precision with which this temperature change could be measured. The precision of measurement of the mass of fuel evaporated was also lower when a small fraction of the fuel was evaporated than when a large fraction was evaporated.

The results are shown graphically in figures 2 and 3, where heat of vaporization is plotted against specific gravity and average volatility, respectively. It is seen from these figures that the data on all the fuels, with the exception of the safety fuel, may be represented,

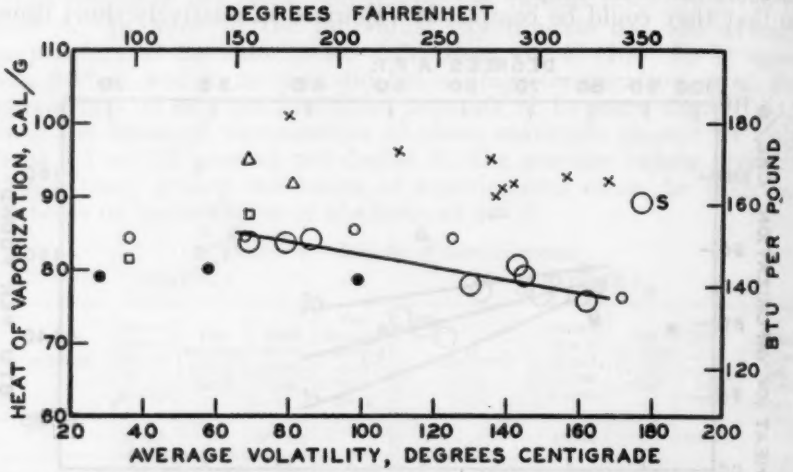

FIGURE 3.—*Heat of vaporization at 40° C plotted against "average volatility."*

○=Fuels. ○S=Safety fuel.
○=Normal paraffins.
●=Isoparaffins.
□=Olefins.
△=Naphthenes.
×=Aromatics.

within the accuracy of the measurements, by a linear function of either specific gravity or average volatility. The average deviation of the observed values from the straight line in figure 3 is somewhat less than from the straight line in figure 2, while the maximum deviation, excepting that for the safety fuel, is somewhat less than 3 percent in both cases.

Curve 1 in figure 2 represents data calculated by means of an equation given by Cragoe [4] for the heats of vaporization of petroleum distillates. Curve 2 represents data calculated by means of equations given by Weir and Eaton [8] for the heat contents of petroleum distillates in the liquid and vapor states.

The values for the heats of vaporization of pure compounds shown in figures 2 and 3 were taken in part from International Critical Tables,[9] and in part from calculations by Young [10] by means of the Clapeyron equation. Where data were found only at temperatures other than 40° C, the reduction to 40° C was made, if sufficient data

[4] Misc. Pub. BS 97 (1929).
[8] Ind Eng. Chem. **24**, 211 (1932).
[9] Int. Crit. Tables **5**, 136.
[10] Sci. Proc. Roy. Dublin Soc. **12**, 374 (1910).

were available, by the method described by Perry and Smith.[11] If sufficient data to use this method were not available, the reduction to 40° C for paraffin hydrocarbons was made using the relation

$$\frac{dL}{dt} = -\frac{0.09}{d}, \tag{2}$$

where L is heat of vaporization, t is temperature, and d is specific gravity at 15° C (or 60° F) referred to water at the same temperature as unity. This relation was obtained by differentiating Cragoe's equation [12] for the heats of vaporization of petroleum distillates. For the aromatic hydrocarbons a similar relation was used, namely,

$$\frac{dL}{dt} = -\frac{0.13}{d} \tag{3}$$

the constant, 0.13, being deduced from the data on benzene by Fiock, Ginnings, and Holton.[13] For the remaining compounds the relation

$$\frac{dL}{dt} = -\frac{0.1}{d} \tag{4}$$

was used. Equation 2 for paraffin hydrocarbons was checked for a number of these compounds, and eq 3 for aromatic compounds was checked for toluene by the method of Perry and Smith.[11] The values of heat of vaporization at 40° C obtained by the two methods agreed in general within 2 percent.

As proposed by Cragoe and Hill,[14] gasolines may be divided for convenience into two classes on a volatility basis. These two classes are aviation gasolines with average volatilities ranging from 80 to 110° C (176 to 230° F), and motor gasolines with average volatilities ranging from 110 to 140° C (230 to 284° F). The variation of heat of vaporization with volatility indicated by the curve of figure 3 is so small that within the accuracy with which the correlation with volatility is valid, the average heat of vaporization for each class of gasolines may be taken as the heat of vaporization of any gasoline in that class. In table 5 are given the average heats of vaporization of aviation and motor gasolines at various temperatures calculated from the heats of vaporization at 104° F by means of eq 2, and heats of vaporization of the safety fuel at various temperatures calculated from the observed heat of vaporization at 104° F by means of eq 3. The values in this table for temperatures other than 100° F are given in parentheses to emphasize the fact that they are calculated, and are therefore not as reliable as the values at 100° F, which are based on observed data.

[11] Ind. Eng. Chem. **25**, 195 (1933).
[12] Misc. Pub. BS 97 (1929).
[13] BS J. Research **6**, 881 (1931) RP312.
[14] BS J. Research **7**, 1133 (1931) RP393.

TABLE 5.—*Heats of vaporization of gasolines*

Temperature	Heat of vaporization		
	Aviation gasoline	Motor gasoline	Safety fuel
	"Average volatility"		
	80 to 110° C (176 to 230° F)	110 to 140° C (230 to 284° F)	177° C (351° F)
° F	Btu/lb	Btu/lb	Btu/lb
0	(161)	(157)	(176)
50	(155)	(151)	(169)
100	148	145	161
150	(142)	(138)	(154)
200	(136)	(132)	(146)
250	(130)	(126)	(139)
300	(123)	(120)	(131)
350	----------	(114)	(124)
400	----------	----------	(116)
450	----------	----------	(109)

In view of the small range covered by the heats of vaporization of the various fuels, it seems probable that appreciable differences in the tendency toward ice formation in the carburetor with different fuels must be due largely to differences in the completeness of vaporization resulting from differences in volatility. The more volatile a fuel the more completely it will be vaporized in the carburetor under given conditions, and the greater will be the heat absorbed per pound of fuel. For example, according to Allen, Rodgers, and Brooks,[15] with an air-fuel ratio of 12, a fuel having an average volatility of 87° C will be 78 percent evaporated in the carburetor at 0° C, while a fuel having an average volatility of 101° C will be only 55 percent evaporated at 0° C. Hence, assuming that the two fuels have about the same heat of vaporization, the more volatile fuel will absorb 42 percent more heat per pound than the less volatile one.

In conclusion the author desires to acknowledge his indebtedness to H. C. Dickinson and C. S. Cragoe for valuable advice during the course of the work. The specific gravities and distillation data on the fuels were determined by H. S. White. The refractive indices were measured by J. D. White. The chemical tests of the safety fuel were made by J. D. White, R. T. Leslie, and F. W. Rose.

WASHINGTON, June 18, 1935.

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[15] Soc. Automotive Engrs. J. **35**, 417 (1934).

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MECHANICAL PROPERTIES OF COTTON YARNS [1]

By Herbert F. Schiefer and Daniel H. Taft

ABSTRACT

The results of tests on three lots of cotton yarns are discussed. Two of the lots (80s and 10s) were spun in the experimental mill of the National Bureau of Standards. The 80s yarn was spun from 1 5/16-inch staple Peeler cotton with 20 different twists. The 10s yarn was spun from 1-inch staple Upland cotton with 12 different twists. Both yarns were spun with right-hand (Z) and with left-hand (S) twist. The third lot was 2/160s mercerized yarn spun from 1¾-inch staple Sea Island cotton. This yarn was considered to be of high commerical quality.

The breaking strength and elongation at rupture were determined by single-strand, multiple-strand, and skein tests. The variation in breaking strength, elongation at rupture, diameter, angle of twist, and irregularity of the 80s and 10s yarns with the amount of twist are shown. The average breaking strength per strand and the elongation by the multiple-strand test are less than those by the single-strand test and greater than those by the skein test. The data were studied statistically and an explanation is given of the differences which were obtained by the different test methods.

Twelve cones of the commercial yarn were tested for breaking strength by the single-strand test. A statistical study of the data indicates significant differences in the average breaking strengths between the different cones.

Some of the factors which affect the strength of a cotton yarn are discussed. The formulas $\tan \beta = \pi DT$ and $T = M\sqrt{C}$ where β, D, T, M, and C are angle of twist, diameter, turns of twist per inch, twist multiplier, and count respectively, are derived by assuming that the exposed fibers are arranged as helices on a circular cylinder and that 2 yarns of different counts have the same density when their angles of twist are equal. It was found that the values for the angle of twist computed by these formulas were consistently greater than the observed values. The empirical formula $\beta = \frac{\arctan \pi DT}{1 - 0.4\sqrt{C}}$, where $T = M\sqrt{C}$, appears to give results which are in good agreement with the observed values.

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[1] The authors express their appreciation to A. A. Mercier, who initiated part of this work, and to J. W. Porter, who assisted in spinning, for their assistance in this investigation before they left the National Bureau of Standards.

I. INTRODUCTION

A cotton yarn is a heterogeneous material. It consists of a large number of individual cotton fibers which are held together by twist. The fibers are not uniform in length, cross section, and strength. They are unequally distributed throughout the length of the yarn. The resulting yarn is irregular and contains hard and soft places, large and small cross sections, and strong and weak places.

A study of the irregularity of cotton yarn has recently been made by Lee.[2] His study is based upon a statistical analysis of the variations in the weight of specimens 6 inches long. The specimens were taken at the various stages during the yarn manufacturing process, from the card sliver to the spun yarn. His results are of great interest since they show the processes where the irregularity is increased or decreased and indicate the processes where improvement in yarn manufacture can be made.

In the experimental study of cotton fabrics at the National Bureau of Standards during the past 5 years a large amount of data has been obtained which shows the effect of twist on the strength, elongation, diameter, angle of twist, and irregularity of cotton yarns. These data are reported and discussed in this paper. The influence of these characteristics on the properties of fabrics woven from these yarns will be reported in 2 subsequent papers.

II. SAMPLES

Two lots of the cotton yarn discussed in this paper were spun in the experimental cotton mill of the Bureau. The third lot of yarn was a commercial product.

Information relative to the cotton and processing of the yarns spun at the Bureau is given in table 1.

TABLE 1.—*Manufacturing details of the cotton yarns spun at the Bureau*

Variety of cotton	Peeler	Upland
Grade	Good middling	Good ordinary
Staple length, inch	1 5/16	1
Breaker picker lap, oz/yd	15	18
Intermediate picker lap, oz/yd		17
Finisher picker lap, oz/yd	12	16
Card sliver, grains/yd	50	64
Sliver lap, grains/yd	484	
Ribbon lap, grains/yd	475	
Comber sliver, grains/yd	55	
First drawing sliver, grains/yd	52	64
Second drawing sliver, grains/yd		59
Finisher drawing sliver, grains/yd	50	53
Slubber roving, hanks/lb [a]	0.50	0.53
Intermediate roving, hanks/lb	1.26	1.26
Second intermediate roving, hanks/lb	4.04	2.10
Jack roving, hanks/lb	15.29	
Yarn, counts [b]	80s (67.2 typp)	10s (8.4 typp).

[a] A hank of cotton roving is equal to 840 yards.

[b] Count is the number of hanks per pound. "Typp" denotes the number of thousand yards per pound. The typp system provides a rational method of designating the size of all yarns, regardless of the kind of fiber composition. It was sponsored by E. D. Fowle in Textile World, **81**, 1,470 (Apr. 23, 1932).

The 80s yarn was spun with 20 different twists. The 10s yarn was spun with 12 different twists. The twist multipliers varied from 2.48 to 6.66 for the 80s yarn and from 2.25 to 9 for the 10s

[2] R. L. Lee, Jr. *A critical study of cotton manufacturing processes*, Textile Research **IV**, no. 5, 235-260 (March 1934); **V** no. 4, 167-183 (February 1935); **V**, no. 7, 326-336 (May 1935).

yarn. The number of turns of twist per inch, T, for each yarn may be calculated by using the formula

$$T=M\sqrt{C}$$

where M is the twist multiplier and C is the cotton count of the yarn. This formula becomes

$$T=M'\sqrt{\text{typp}}$$

for the typp system, where $M'=1.091\ M$. Because of the familiarity of cotton spinners and weavers with the twist multipliers which are associated with the cotton count and because of the practical applications of the results to be presented, the cotton count is used in this paper instead of the typp system.

The 80s yarn was spun from double roving, using right-hand (Z) and left-hand (S) twist for each twist multiplier. The 10s yarn was spun from single and from double roving for each twist multiplier, using right-hand (Z) and left-hand (S) twist. The draft was increased in the spinning process as the twist was increased to keep the yarn counts as near 80s and 10s as practicable.

The relative humidity was maintained at approximately 65 percent during the manufacturing of these yarns.

The third type of yarn studied was a 2/160s commercial yarn spun from 1¾ inch staple Sea Island cotton. The 160s (134.4 typp) yarn was spun with a twist multiplier of 3.5 (44 turns of twist per inch). A twist multiplier of 4.4 (37 turns of twist per inch) was used in plying. The plied yarn was mercerized. This yarn was considered to be of high commercial quality.

III. TEST PROCEDURE

1. BREAKING STRENGTH AND ELONGATION AT RUPTURE

The breaking strength and elongation at rupture of the yarns were determined by the single-strand, multiple-strand, and skein tests. The tests were made on material which was exposed for at least 4 hours to an atmosphere of 65 percent relative humidity and 70° F.

In the single-strand test the yarn was clamped in the small jaws of a pendulum type machine, having 2 capacities of 18 and 36 ounces, respectively. The distance between the jaws was 4 inches and the jaws were separated at a rate of 4 inches per minute. In this test it is important to clamp the yarn with a small and uniform tension.[3] The procedure adopted was to apply sufficient tension on the yarn to cause the freely swinging pendulum to move slightly from its vertical position. The breaking strength and elongation at rupture were read from the scales of the machine. At least 50 determinations were made for each direction of twist and twist multiplier of the yarns.

[3] In some testing machines means are provided for clamping the pendulum in a vertical position while inserting the sample in the jaws of the machine. Clamping the pendulum in a vertical position while inserting the samples leads to erroneous results, especially in elongation. It has been found that the apparent elongation of the yarn is decreased by the considerable and variable tension under which the specimen is likely to be mounted under these conditions.

In the multiple-strand test [4] 100 strands were wound parallel on a split frame with a slight and uniform tension. The strands and frame were clamped in the jaws of a pendulum type of machine having a capacity of 150 pounds. The distance between the jaws was 4 inches and the jaws were separated at the rate of 12 inches per minute. The breaking strength and elongation at rupture were obtained from the curves drawn by the machine. At least 10 determinations were made for each direction of twist and twist multiplier of the yarns.

In the skein test 120 yards of yarn were wound on a reel having a perimeter of 1½ yards. This skein, consisting of 80 loops or 160 strands, was then placed on the 2 drums of a pendulum type of machine having a capacity of 150 pounds. The drums were 1 inch in diameter and were separated at the rate of 12 inches per minute. The breaking strength and elongation at rupture were obtained from the curves drawn by the machine. At least 10 determinations were made for each direction of twist and twist multiplier of the yarns.

2. DIAMETER AND ANGLE OF TWIST

The diameter of the yarn and the angle of twist, that is the angle at which the individual fibers appear to be inclined to the longitudinal axis of the yarn, were measured with a rotary stage microscope and micrometer. The yarn was wound without tension on a strip of black cardboard 1 inch wide. At least 10 determinations were made for each direction of twist and twist multiplier of the yarns.

3. FORMULAS [5]

The following formulas were used in computing the average, standard deviation, coefficient of variation, and their standard errors from the frequency distributions. N is the number of determinations, I is the class interval of the frequency distribution, f is the frequency in each class interval, m is the class interval midpoint taken as the assumed average, and d is the number of deviation steps a class interval is from m.

Average, A,

$$A=m+sI,$$

where m=an assumed average and $s=\frac{\Sigma\,(f\,d)}{N}$

Standard deviation, σ,

$$\sigma=I\sqrt{\frac{\Sigma(f\,d^2)}{N}-s^2}$$

[4] C. W. Schoffstall and H. A. Hamm, *A multiple-strand test for yarns*, BS J. Research **2**, 871 (1929) RP61. When this test method was developed it was customary to line the jaws of the testing machine with strips of rubber about 1/10 inch thick. This practice leads to erroneous results, especially in elongation. It was found that the apparent elongation of the yarn was greatly increased by an amount dependent upon the breaking load, the effect being due to the elongation of the rubber. The rubber was not used in the tests reported in this paper.

[5] The mathematical treatment may be found in the following texts. E. E. Day, Statistical Analysis (MacMillan & Co.); M. Ezekiel, Methods of Correlation Analysis (John Wiley & Sons); F. C. Mills, Statistical Methods (Henry Holt & Co.); C. H. Forsyth, Mathematical Analysis of Statistics (John Wiley & Sons); W. A. Shewhart, Economic Control of Quality of Manufactured Products (D. Van Nostrand Co.).

Coefficient of variation, V,

$$V=\frac{100\sigma}{A}$$

Standard error of the average, σ_A,

$$\sigma_A=\frac{\sigma}{\sqrt{N-1}}$$

Standard error of the coefficient of variation, σ_V,

$$\sigma_V=\frac{V\sqrt{1+2(0.01V)^2}}{\sqrt{2(N-1)}}$$

The coefficient of variation is taken as an indication of the irregularity of the yarn with respect to that property which is being considered. The standard error of the difference between two measures, σ_Δ, is the square root of the sum of the squares of the standard errors of the two measures. The difference between the two measures, Δ, divided by the standard error of the difference is taken as the significance ratio R. In statistical analysis a value of R greater than 3 is an indication of a significant difference between the two measures. This criterion has been adopted in this paper.

IV. RESULTS

1. BUREAU'S 80s (67.2 TYPP) COTTON YARN

There appeared to be no consistent differences in the data for the yarns spun with right-hand and left-hand twist for the various twist multipliers. No distinction is therefore made in the results presented.

The variations in breaking strength and in elongation at rupture by the single-strand test for the various twist multipliers are shown by frequency distributions in tables 2 and 3, respectively. The tables also contain the average, standard deviation, and coefficient of variation for the various twist multipliers.

The average breaking strength increases with an increase in twist multiplier to a maximum at a twist multiplier of about 3.33 and then decreases. The coefficient of variation decreases in general with an increase in twist multiplier to a minimum at a twist multiplier of about 3.67 and then increases. The standard error of the coefficient of variations, the difference between the coefficient of variation at twist multiplier 3.67 and the coefficient of variation for the other twist multipliers, the standard error of these differences, and the significance ratio of the differences are also given in table 2.

TABLE 2.—*Frequency distribution of breaking strength of 80s cotton yarn by the single-strand test*

Breaking strength (in oz.) at cell midpoint	Twist multiplier									
	2.48	2.71	2.93	3.19	3.26	3.33	3.41	3.49	3.58	3.67
2.8	4									
3.1	7			6						
3.4	26	11		8	3					4
3.7	20	16	20	11	14		7	7	14	10
4.0	16	23	20	11	21	5	15	12	13	14
4.3	18	18	29	22	14	22	17	27	25	26
4.6	9	15	17	13	10	26	22	19	14	23
4.9		9	8	10	12	22	18	10	19	14
5.2		7	5	11	14	10	12	15	7	6
5.5		1	1	6	6	5	5	10	2	3
5.8				2	6	7	2		4	
6.1						2	2		2	
6.4						1				
Total	100	100	100	100	100	100	100	100	100	100
Average, *A*, oz.	3.78	4.21	4.28	4.36	4.52	4.81	4.62	4.59	4.52	4.41
Standard deviation, oz.	.477	.522	.435	.681	.660	.537	.546	.519	.579	.483
Coef of var., *V*, %	12.6±	12.4±	10.2±	15.6±	14.6±	11.2±	11.8±	11.3±	12.8±	11.0±
	0.91	0.89	0.74	1.13	1.06	0.81	0.85	0.81	0.92	0.79
$\Delta = V - 11.0$, %	1.6±	1.4±	−0.8±	4.6±	3.6±	0.2±	0.8±	0.3±	1.8±	0.0±
	1.21	1.19	1.08	1.38	1.32	1.13	1.16	1.13	1.21	1.12
Significance ratio, *R*	1.3	1.2	−0.7	3.2	2.7	0.2	0.7	0.3	1.5	0

Breaking strength (in oz.) at cell midpoint	Twist multiplier									
	3.76	3.86	3.96	4.07	4.58	5.05	5.64	6.11	6.37	6.66
2.5								4	6	9
2.8					6	2		13	4	17
3.1	2	1	6	5	4	17	5	11	18	22
3.4	7	7	6	7	9	9	14	14	22	20
3.7	16	14	7	19	16	15	14	12	10	20
4.0	16	19	29	18	16	17	18	7	6	6
4.3	11	18	16	13	14	8	16	7	12	5
4.6	19	21	11	16	7	8	10	12	12	1
4.9	12	10	16	10	11	3	8	4	4	
5.2	12	8	4	8	5	9	8	8	4	
5.5	5	2	3	4	4	8	6	4	0	
5.8			2		6	4	1	3	2	
6.1					2			1		
Total	100	100	100	100	100	100	100	100	100	00
Average, *A*, oz.	4.37	4.30	4.28	4.27	4.24	4.12	4.21	3.93	3.77	3.30
Standard deviation, oz.	.618	.525	.612	.618	.825	.834	.675	.921	.772	.477
Coef of var., *V*, %	14.2±	12.2±	14.3±	14.6±	19.4±	20.2±	16.0±	23.5±	20.5±	14.4±
	1.03	0.88	1.04	1.06	1.43	1.49	1.16	1.76	1.52	1.05
$\Delta = V - 11.0$, %	3.2±	1.2±	3.3±	3.6±	8.4±	9.2±	5.0±	12.5±	9.5±	3.4±
	1.30	1.18	1.31	1.32	1.63	1.60	1.40	1.93	1.71	1.31
Significance ratio, *R*	2.5	1.0	2.5	2.7	5.2	5.4	3.6	6.5	5.6	2.6

The average elongation at rupture increases with an increase in twist multiplier. The coefficient of variation of the elongation, however, decreases slightly with an increase in twist multiplier to a minimum at twist multiplier 3.67 and then increases considerably for higher twist multipliers. The standard error of the coefficient of variations, the difference between the minimum coefficient of variation at twist multiplier 3.67 and the coefficient of variation for the other twist multipliers, the standard error of these differences, and the significance ratio of the differences are also given in table 3.

TABLE 3.—*Frequency distribution of elongation of 80s cotton yarn by the single-strand test*

Elongation (in %) at cell midpoint	Twist multiplier—									
	2.48	2.71	2.93	3.19	3.26	3.33	3.41	3.49	3.58	3.67
4.75	2									
5.15	11									
5.55	17	2	6	4						
5.95	40	34	19	15	5	1		1		
6.35	21	32	28	13	18	12	3	5		
6.75	9	11	19	32	21	21	9	12	6	7
7.15		19	21	24	26	22	35	17	28	22
7.55		2	7	6	18	23	25	27	28	42
7.95				4	9	17	25	29	28	20
8.35				2	3	4	3	6	6	9
8.75								3	4	
Total	100	100	100	100	100	100	100	100	100	100
Average, A, %	5.93	6.42	6.55	6.75	7.04	7.23	7.43	7.51	7.60	7.56
Standard deviation, %	.468	.480	.540	.588	.584	.568	.448	5.72	.472	.412
Coef of var., V, %	7.9±	7.5±	8.2±	8.7±	8.3±	7.9±	6.0±	7.6±	6.2±	5.4±
	0.56	0.54	0.59	0.62	0.59	0.56	0.43	0.54	0.44	0.38
$\triangle = V - 5.4$, %	2.5±	2.1±	2.8±	3.3±	2.9±	2.5±	0.6±	2.2±	0.8±	0.0±
	0.68	0.66	0.70	0.73	0.70	0.68	0.57	0.66	0.59	0.54
Significance ratio, R	3.7	3.2	4.0	4.5	4.1	3.7	1.1	3.3	1.4	0

Elongation (in %) at cell midpoint	Twist multiplier—									
	3.76	3.86	3.96	4.07	4.58	5.05	5.64	6.11	6.37	6.66
5.95	1	1	1							
6.35	0	2	2							
6.75	4	3	8	2		5				
7.15	23	14	18	14	12	9	5	6	3	
7.55	29	26	14	12	6	3	4	0	0	
7.95	21	28	28	41	12	8	6	4	4	1
8.35	10	13	8	13	17	8	3	4	3	1
8.75	9	10	7	16	18	13	7	8	6	3
9.15	3	3	12	2	15	11	12	7	12	6
9.55			2		10	9	10	9	8	6
9.95					8	9	13	14	20	10
10.35					2	11	13	10	12	9
10.75						6	15	7	11	6
11.15						7	7	3	1	10
11.55						1	4	7	4	9
11.95							1	11	8	15
12.35								8	6	5
12.75								0	0	5
13.15								2	2	7
13.55										2
13.95										2
14.35										0
14.75										3
Total	100	100	100	100	100	100	100	100	100	100
Average, A, %	7.73	7.81	7.87	7.97	8.59	9.09	9.67	10.17	10.12	11.23
Standard deviation, %	.600	.612	.788	.536	.852	1.276	1.188	1.500	1.304	1.484
Coef of var., V, %	7.8±	7.8±	10.0±	6.7±	10.1±	14.0±	12.3±	14.7±	12.9±	13.3±
	0.76	0.76	0.72	0.48	0.73	1.01	0.89	1.06	0.93	0.96
$\triangle = V - 5.4$, %	2.4±	2.4±	4.6±	1.3±	4.7±	8.6±	6.9±	9.3±	7.5±	7.9±
	0.85	0.85	0.81	0.61	0.82	1.08	0.97	1.13	1.04	1.03
Significance ratio, R	2.8	2.8	5.7	2.1	5.7	8.0	7.1	8.2	7.2	7.7

The strength, elongation, and irregularity of the 80s cotton yarn vary with the twist multiplier. The irregularity based upon strength and upon elongation is least for twist multiplier 3.67 and highest for twist multiplier 6.11. This change is shown very strikingly by the scatter diagrams shown in figure 1 where the strength is plotted against the elongation for the single-strand tests of the yarn of twist multipliers 2.48, 3.67, and 6.11. The coefficient of variation for strength and elongation are given in figure 1 for each twist multiplier and the average strength and elongation are indicated.

In the multiple-strand test, 100 strands, each 4 inches long, are subjected to tension simultaneously and all strands are elongated ally as tension is applied. The scatter diagrams of figure 1 show that there is a considerable variation in the elongation at rupture

between the separate strands. In the multiple-strand test the strands having the lowest elongation at rupture are broken first and the load carried by them must then be assumed by the unbroken strands which break at higher elongations and which at this moment carry only a fraction of their ultimate breaking load. After several strands are broken the total load carried by the unbroken strands reaches a maximum value which is sufficient to break all of the remaining strands in rapid succession as soon as an additional strand is broken. This maximum load carried by the aggregate of the strands is taken as the breaking strength of the 100 strands. The average breaking strength per strand of 100 strands by the multiple-strand test is obviously less than the average breaking strength per strand obtained by testing 100 strands by the single-strand test because the maximum load is carried by less than 100 strands in the multiple-strand test and because the unbroken strands which have a

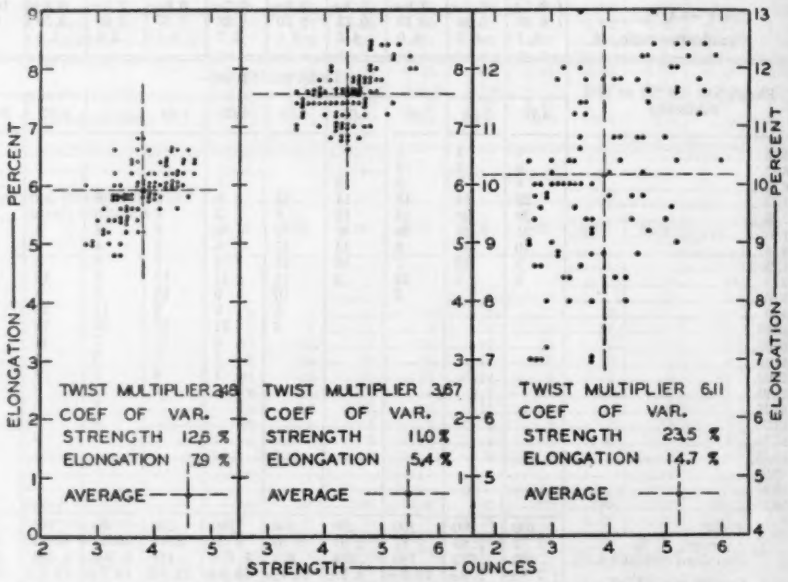

FIGURE 1.—*Scatter diagrams for three-twist multipliers of 80s cotton yarn.*

high elongation at rupture, carry a load less than their ultimate breaking strength when the load carried by the aggregate is a maximum. The ratio of the average breaking strength per strand by the multiple-strand test to the average breaking strength per strand by the single-strand test is a fraction which decreases, in general, with an increase in twist multiplier. This decrease is readily explained by the variation in the irregularity of the yarn with respect to elongation at rupture, which is measured by the coefficient of variation and takes into consideration the variations of both the magnitude and the spread of the elongation at rupture with an increase in twist multiplier. It should be noted that the single-strand tests were made at a lower speed than the multiple-strand tests. This factor may have some effect on the results.

Similar variations are also found for average elongation by the two methods of test, where elongation by the multiple-strand test refers

to the elongation corresponding to the maximum load carried by the 100 strands.

In the regular skein test, 160 strands, 80 loops, are subjected to tension simultaneously. Each strand is in effect 27 inches long. On the basis of the discussion given above for the multiple-strand test the average breaking strength per strand and the elongation at the maximum load carried by the skein are expected to be lower than those

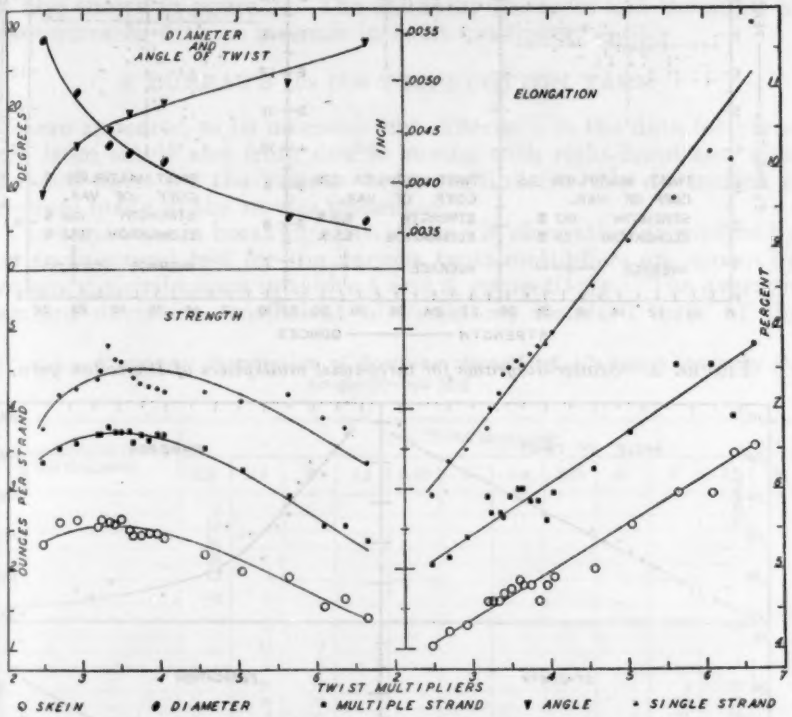

FIGURE 2.—*Effect of twist multiplier on the breaking strength, elongation at rupture, diameter, and angle of twist of the 80s cotton yarn.*

The differences in the results obtained by the three methods of determining the strength and elongation are also shown.

obtained by the single-strand test. An additional reduction is to be expected because the variations occurring in specimens 27 inches long are greater than those found in specimens only 4 inches long. The ratio of the average breaking strength per strand by the skein test to the average breaking strength per strand by the single-strand or by the multiple-strand test is a fraction which decreases in general with an increase in twist multiplier.

The results for strength and elongation by the three methods of test are plotted in figure 2 against twist multiplier. The graphs indicate the variation of strength and elongation with twist multiplier for

each method of test as well as the relationship for strength and elongation between the three methods of test. The maximum strength by

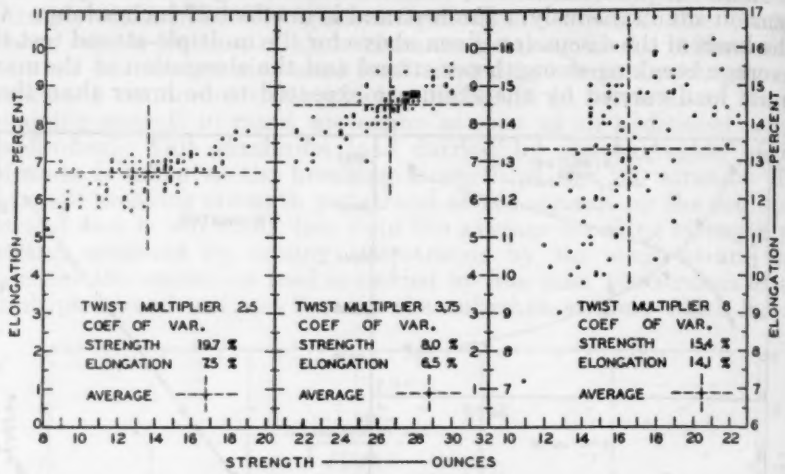

FIGURE 3.—*Scatter diagrams for three-twist multipliers of 10s cotton yarn.*

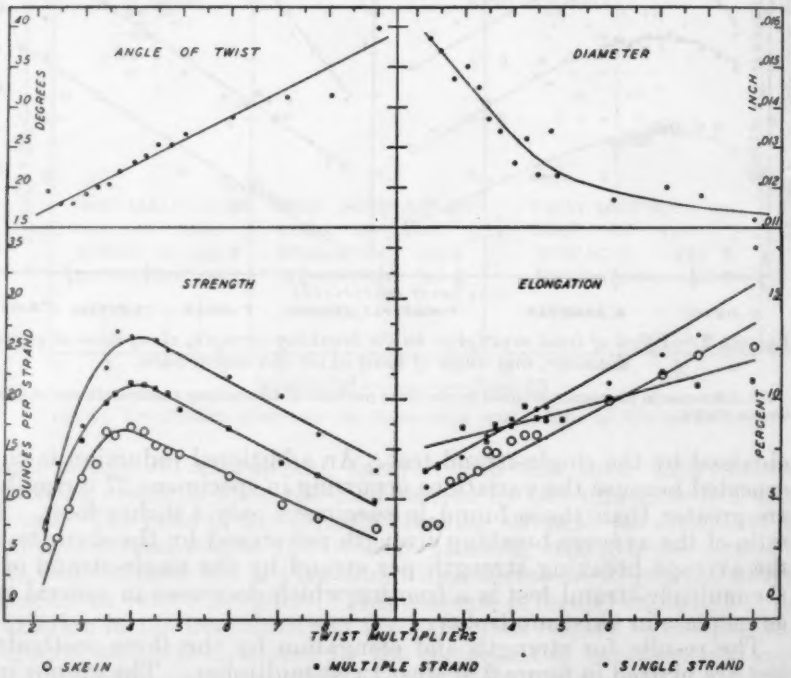

FIGURE 4.—*Effect of twist multiplier on the breaking strength, elongation at rupture, diameter, and angle of twist of the 10s cotton yarn.*

The differences in the results obtained by the three methods of determining the strength and elongation are also shown.

the multiple-strand and skein tests appears to occur at a slightly lower twist multiplier than for the single-strand test. This is in agreement

with the shift noted by Mercier [6] for combed and carded cotton yarns. He reported maximum strength at twist multiplier 5.25 for the single-strand test and at 4.25 for the skein test of the same yarns. This shift can be explained on the basis of an increase in irregularity of the yarn with respect to elongation as the twist multiplier is increased. Unfortunately Mercier did not investigate this property in his study.

The variations of diameter and angle of twist with twist multiplier are also shown in figure 2. The diameter decreases and the angle of twist increases with an increase in twist multiplier.

2. BUREAU'S 10s (8.4 TYPP) COTTON YARN

There appeared to be no consistent difference in the data for yarns spun from single and from double roving with right-hand and with left-hand twist for the various twist multipliers. No distinction is therefore made in the results presented.

The variations in breaking strength and in elongation at rupture by the single-strand test for the various twist multipliers are shown by frequency distributions in tables 4 and 5, respectively. The average, standard deviation, coefficient of variation, standard error of the

TABLE 4.—*Frequency distribution of breaking strength of 10s cotton yarn by the single-strand test*

Breaking strength (in oz) at cell midpoint	Twist multiplier											
	2.25	2.5	3	3.5	3.75	4	4.5	4.75	6	7	8	9
4.5	5											
5.5	14											
6.5	34											
7.5	26											
8.5	15	4										1
9.5	6	9										6
10.5		5									1	19
11.5		9									0	13
12.5		15	2								4	10
13.5		9	1								6	24
14.5		20	12						1	4	18	10
15.5		10	19						4	12	19	6
16.5		6	21						3	11	18	8
17.5		9	9					1	5	11	6	1
18.5		2	11	2				0	3	15	9	1
19.5		2	12	7				1	10	12	9	1
20.5			4	10				6	10	10	1	
21.5			6	12	4	3	11	9	11	8	5	
22.5			3	17	5	7	10	13	13	3	4	
23.5				15	1	5	9	7	8	2		
24.5				13	10	15	10	15	14	6		
25.5				12	7	17	15	13	6	2		
26.5				7	20	16	13	13	5	2		
27.5				5	32	16	5	8	1	2		
28.5					6	10	7	4	3			
29.5					10	6	10	3	1			
30.5					5	3	5	4	0			
31.5						2	2	3	1			
32.5							3		1			
Total	100	100	100	100	100	100	100	100	100	100	100	100
Average, *A*, oz	7.0	13.6	17.3	23.2	26.7	26.2	25.9	24.9	22.2	19.3	16.6	12.9
Standard deviation, oz	1.22	2.68	2.30	2.26	2.13	2.26	3.04	2.93	3.50	3.08	2.55	2.24
Coef of var., *V*, %—	17.4±	19.7±	13.4±	9.7±	8.0±	8.6±	11.8±	11.8±	15.8±	16.0±	15.4±	17.4±
	1.27	1.45	0.97	0.69	0.57	0.62	0.85	0.85	1.15	1.16	1.12	1.27
$\Delta = V - 8.0$, %	9.4±	11.7±	5.4±	1.7±	0.0±	0.6±	3.8±	3.8±	7.8±	8.0±	7.4±	9.4±
	1.40	1.56	1.13	0.89	0.81	0.84	1.02	1.02	1.28	1.29	1.26	1.40
Significance ratio, *R*	6.7	7.5	4.8	1.9	0	0.7	3.7	3.7	6.1	6.2	5.9	6.4

[6] A. A. Mercier and C. W. Schoffstall, *Effect of twist on cotton yarns*. BS J. Research 1, 733 (1928) RP27.

TABLE 5.—*Frequency distribution of elongation of 10s cotton yarn by the single-strand test*

Elongation (in %) at cell midpoint	Twist multiplier											
	2.25	2.5	3	3.5	3.75	4	4.5	4.75	6	7	8	9
4.75	6											
5.25	30	1										
5.75	48	8	1									
6.25	14	23	14									
6.75	2	35	20	2	1							
7.25		31	41	6	5		1	1			1	
7.75		2	12	16	9	3	0	0			0	
8.25			12	49	33	20	9	4			0	
8.75				17	36	23	10	11			0	
9.25				9	15	27	31	31	2		0	
9.75				1	1	18	23	16	9		1	
10.25						9	20	23	26	7	8	
10.75							3	10	17	6	4	
11.25							3	3	24	15	6	
11.75								0	7	7	3	
12.25								1	14	27	11	
12.75									1	4	6	
13.25										17	11	
13.75										9	3	1
14.25										7	17	4
14.75										1	8	4
15.25											11	12
15.75											3	6
16.25											5	8
16.75											2	3
17.25												13
17.75												11
18.25												11
18.75												2
19.25												7
19.75												5
20.25												3
20.75												2
21.25												3
21.75												2
22.25												1
22.75												2
Total	100	100	100	100	100	100	100	100	100	100	100	100
Average, A, %	5.63	6.72	7.18	8.27	8.49	9.07	9.51	9.69	10.92	12.33	13.33	17.76
Standard deviation, %	0.42	0.51	0.60	0.55	0.55	0.65	0.73	0.79	0.81	1.14	1.68	2.09
Coef of var., V, %	7.4±	7.5±	8.3±	6.6±	6.5±	7.2±	7.7±	8.2±	7.4±	9.2±	14.1±	11.8±
	0.53	0.54	0.59	0.47	0.46	0.51	0.55	0.59	0.53	0.65	1.02	0.85
$\Delta = V - 6.5$, %	0.9±	1.0±	1.8±	0.1±	0.0±	0.7±	1.2±	1.7±	0.9±	2.7±	7.6±	5.3±
	0.70	0.71	0.75	0.66	0.65	0.69	0.72	0.75	0.70	0.80	1.12	0.97
Significance ratio, R	1.3	1.4	2.4	0.2	0	1.0	1.7	2.3	1.3	3.4	6.8	5.5

coefficient of variation, the difference between the minimum coefficient of variation at twist multiplier 3.75 and the coefficient of variation for the other twist multipliers, the standard error of these differences, and the significance ratio of these differences are also given in the tables for the various twist multipliers. The scatter diagrams shown in figure 3 are for twist multipliers 2.5, 3.75, and 8. The results for strength and elongation by the three methods of tests are plotted in figure 4 against twist multiplier. The variations in diameter and angle of twist with twist multiplier are also shown in figure 4.

In general, the same conclusions may be drawn from these results as were made for the 80s cotton yarns. They are not discussed individually for the sake of brevity.

3. COMMERCIAL COTTON YARN, 2/160s (2/134.4 TYPP)

Forty pounds of 2/160s mercerized cotton yarn of high commercial quality were purchased for a study of cotton fabrics for parachutes. One hundred breaking-strength determinations were made by the

single-strand test on each of 12 cones of yarn selected at random from the entire lot. The variations in breaking strength of the yarn from the different cones and from the entire lot are shown by frequency distributions in table 6. The average, standard error of the average, standard deviation, coefficient of variation, difference between average of cone no. 1 and average of the other cones, and the standard error and significance ratio of these differences are also given in table 6.

TABLE 6.—*Frequency distribution of breaking strength for 12 cones of 2/160s mercerized cotton yarn of high commercial quality*

Breaking strength (in oz) at cell midpoint	Cone numbers												
	1	2	3	4	5	6	7	8	9	10	11	12	1 to 12, incl.
3.5	1												1
4.0	1								1				2
4.5	0	2				1			0				3
5.0	2	1	1			0	3	1	0		2		10
5.5	2	3	2	4	2	2	1	1	2	1	2	1	23
6.0	8	9	9	7	4	6	4	5	5	4	6	5	72
6.5	15	12	15	8	17	10	7	7	6	6	10	10	123
7.0	23	14	17	22	18	18	17	7	13	10	12	10	181
7.5	18	24	20	21	22	23	22	23	19	24	11	10	237
8.0	10	7	18	17	9	10	15	6	13	12	10	10	137
8.5	14	12	3	7	9	10	11	28	13	17	9	14	147
9.0	4	7	6	6	7	10	10	12	11	8	13	17	111
9.5	2	7	6	6	8	5	9	7	5	10	10	9	84
10.0		2	2	2	1	3	1	2	6	5	10	7	41
10.5			1		2	2		1	6	2	3	4	21
11.0					1					0	2	1	4
11.5										1		2	3
Total	100	100	100	100	100	100	100	100	100	100	100	100	1,200
Average, A, oz.	7.24±	7.48±	7.48±	7.54±	7.66±	7.69±	7.73±	7.98±	8.02±	8.09±	8.11±	8.29±	7.774±
	0.108	0.120	0.120	0.104	0.116	0.117	0.109	0.107	0.130	0.111	0.144	0.135	0.122
Standard deviation, oz.	1.07	1.19	1.19	1.03	1.15	1.16	1.08	1.06	1.29	1.10	1.43	1.34	1.215
Coef of var., V, %	14.8	15.9	15.9	13.7	15.0	15.1	14.0	13.3	16.1	13.6	17.6	16.2	15.7
$\Delta=A-7.24$, oz.	0.00±	0.24±	0.24±	0.30±	0.42±	0.45±	0.49±	0.74±	0.78±	0.85±	0.87±	1.05±	0.534±
	0.152	0.161	0.161	0.149	0.158	0.158	0.153	0.151	0.168	0.154	0.180	0.172	0.163
Significance ratio, R	0	1.5	1.5	2.0	2.7	2.9	3.2	4.9	4.7	5.5	4.8	6.1	3.3

The average breaking strength varies from 7.24 ounces for cone no. 1 to 8.29 ounces for cone no. 12. This variation is 13.5 percent of the average of 7.774 ounces for the entire lot and the difference between 7.24 and 8.29 ounces is 6.1 times its standard error, which is a significant difference. On the other hand the significance ratios of the differences between the average breaking strengths of cones nos. 1 and 12 and the average of the entire lot are 3.3 and 2.8, respectively. These values are close to the limiting value indicating a significance.

The coefficient of variation, which is taken as a measure of irregularity, varies from 13.3 to 17.6 percent between the different cones and is equal to 15.7 percent for the entire lot. This is somewhat higher than the irregularity of about 10 to 12 percent obtained for the 80s and 10s yarn for the twist multipliers yielding maximum strength. On the assumption that the single unmercerized yarn had the same irregularity as the Bureau's yarn it appears that plying and mercerization did not decrease the irregularity of this yarn materially. A more extensive study of the effect of these factors on the irregularity of the yarn must be made, however, to establish this fact.

V. FACTORS AFFECTING THE STRENGTH OF A COTTON YARN

The strength, length, and other characteristics of the cotton fibers have an effect on the strength of a cotton yarn. The relation of yarn strength to fiber strength has been discussed in considerable detail by Turner.[7] The strength of the yarn is related to the length of the cotton fiber. For example, it was found that a 10s yarn spun from the $1\frac{5}{16}$-inch staple Peeler cotton had a breaking strength 63 percent greater than a 10s yarn spun with the same twist multiplier from the 1-inch staple Upland cotton. Similarly it is known that a combed yarn is stronger than a carded yarn spun from the same raw cotton because many of the shorter and inferior fibers are removed in the combing process.

The effect of twist on the strength of the yarn is indicated in this paper and confirms the results obtained in previous investigations. Imparting twist to a bundle of cotton fibers decreases the diameter of the bundle, that is, it brings the fibers in closer contact by a radial pressure, thereby increasing the frictional forces between fibers or the resistance of fiber slippage when tension is applied to the bundle. On the other hand twist introduces torsional forces or shearing stresses in the individual fibers thereby decreasing their breaking strength in tension. A moderate amount of twist reduces the diameter a considerable amount and therefore increases the frictional forces between the fibers, while it does not set up appreciable stresses in the fibers or produce an appreciable decrease in the breaking strength of the fibers in tension.[8] It is expected therefore that the strength of the yarn should increase very materially to a maximum with a moderate increase in twist. Additional increase in twist decreases the diameter slightly and the effects of the opposing strength factors balance each other approximately, producing relatively little change in the strength of the yarn from the maximum value. At high twist, however, the increase in the friction between fibers due to an increase in twist or a decrease in diameter is negligible while the decrease in the fiber strength due to internal stresses becomes appreciable. The strength of the yarn decreases rapidly with an increase in high twist and for excessively high twist the yarn may break during the twisting process without the addition of any external tension.

Two other factors are also operative in materially reducing the breaking strength of yarns at high twist relative to the breaking strength at low twist. They are (1) increase in the draft during spinning of yarns of high twist and (2) variation in twist between fibers near the axis and the surface of the yarn.

Increasing the draft for high twist to keep the count of the yarn at no tension constant has the same effect as reducing the weight per unit length of the yarn when it is under a tension substantially equal to its breaking strength. The decrease is proportional to the difference in elongation at rupture between a low-twisted and a high-twisted yarn.

The fibers located near the axis of the yarn are not twisted to the same degree as those near the surface. This difference increases

[7] A. J. Turner, *The foundation of yarn strength and yarn extension.* J. Textile Inst. **19**, T286–T314 (1928).
[8] H. A. Hamm and R. S. Cleveland, *Relation between the twist and certain properties of rayon yarns*, BS J. Research **7**, 617 (1931) RP361.

with twist. When tension is applied to yarn the fibers near the surface assume less of the load because of greater twist (greater elongation) than the fibers near the axis. For higher and higher twist this difference increases and the fibers near the surface become less and less effective.

The data in the literature seem to indicate that maximum strength of fine yarns is obtained at lower twist multipliers than in coarse yarn. Furthermore, a yarn appears to increase in strength more rapidly than its weight, that is, a 20s yarn has in general a breaking strength more than twice as great as that of a 40s yarn. These observations may be explained as follows: A fine yarn is usually spun from longer staple fiber and the ratio of the circumference of the yarn to the area of its cross section is greater in fine yarns than in coarse yarns. The longer fibers require less twist to increase the resistance of fiber slippage and the fibers retain more of their initial strength because the internal stresses due to twist are still small. Because of the greater ratio of the circumference to the cross-sectional area a smaller percentage of the total number of fibers are completely imbedded in the yarn or a greater percentage are exposed at the surface. The increase in twist cannot increase the frictional resistance of the fibers exposed at the surface. Both of these factors tend to produce maximum strength at lower twist multipliers. They explain why maximum strength is obtained at a lower twist multiplier in fine yarn than in coarse yarn.

The second factor explains why a 20s yarn, for example, has a breaking strength equal to more than twice that of a 40s yarn spun from the same raw cotton. The cross-sectional area of the 20s yarn is twice that of the 40s yarn, while the circumference of the 20s yarn is only 1.414 times that of the 40s yarn. Because a greater percentage of the total number of fibers are exposed on the surface in fine yarns and are therefore comparatively ineffective, it is apparent why the breaking strength increases at a greater rate than the rate of increase in weight, all other factors remaining constant.

VI. RELATIONS BETWEEN DIAMETER, ANGLE OF TWIST, COUNT, AND TWIST

A direct relationship between diameter and angle of twist with twist multiplier has been indicated for 2 counts in this paper. In fact the formula $T=M\sqrt{C}$, which has been used for many years and was presented by Joseph Köchlin on November 28, 1828, before the Société Industrielle de Mulhouse,[9] expresses a simple relationship between the count, twist multiplier, and number of turns of twist per inch. This formula can be readily derived by assuming that the exposed fibers are arranged as helices on a circular cylinder and that 2 yarns of different count have the same density when their angles of twist are equal. The projection of a helix on the xy-plane may be expressed by the equation

$$y=D/2 \sin 2\pi Tx$$

where the x-axis coincides with the axis of the cylinder, D is the diameter and T is the number of turns of twist per inch. The angle

[9] H. Brüggemann, Zwirne, p. 103 (1933). Published by R. Oldenbourg, Munich and Berlin, Germany,

of twist is by definition equal to the angle which a tangent line makes with the x-axis at the origin of the above curve. If β is the angle of twist, then it follows by differentiation that

$$dy/dx = \tan \beta = \pi DT \text{ when } x=0$$

Let D and T represent the diameter and number of turns of twist per inch of a yarn of count C and D' and T' similar values of a yarn of count C'. If these 2 yarns have the same angle of twist then

$$T = T'D'/D.$$

If w represents the weight per unit length of yarn of count C, δ the density, and k a constant, then

$$k/C = w = \pi \delta l D^2/4 \text{ and } k/C' = w' = \pi \delta' l D'^2/4,$$

since the count is inversely proportional to the weight. It follows therefore that

$$D'/D = \sqrt{\delta/\delta' \cdot C/C'} \text{ and } T = T'/\sqrt{C'} \cdot \sqrt{C}$$

on the assumption that $\delta = \delta'$ when $\beta = \beta'$. The expression $T'/\sqrt{C'}$ is ordinarily termed the twist multiplier M and represents the number of turns of twist per inch in a yarn of count unity, $C'=1$. It is interesting to note that in Köchlin's derivation the additional assumption is made that the coefficient of friction between fibers is the same in yarns of different count when the exposed fibers make the same angle of twist. Köchlin expressed the coefficient of friction as equal to the tangent of the angle of twist. This expression is analogous to the common way of expressing the coefficient of friction between two surfaces. This assumption is very interesting and probably applies to the surfaces of the exposed fibers. It is not necessary, however, in the derivation of the above formula.

In A of figure 5 are plotted the observed values of the angle of twist for 10s, 80s,[10] 100s,[11] and 120s[12] yarn against the values computed from the formula $\tan \beta = \pi DT$ in which D was taken equal to observed diameters and T, the number of turns of twist per inch, was computed by the formula $T = M\sqrt{C}$. It is seen that the computed values are consistently greater than the observed values and the difference appears to increase with the count of the yarn. This indicates that the assumptions made in the above formulas are not strictly fulfilled in spun yarns. From the data at hand it is not possible to determine which assumption is in error. In fact it would be very difficult to determine because the yarn is irregular in other properties and probably varies as much in helical arrangement of the fibers, form of the cross section, and density. On the basis of experimental data Wagner and Herzog[13] have derived the empirical formula $\tan \beta = 0.873\ \pi DT$. The computed values of β for 10s yarn by this formula are in excellent agreement with the observed values,

[10] [11] [12] These yarns were spun from the same cotton.

[13] P. Heermann und A. Herzog, Mikroskopische und mechanisch-technische Textiluntersuchungen, p. 233, Dritte Auflage (1931). Published by Julius Springer, Berlin, Germany.

but the agreement is not very good for yarns of higher counts (see B of fig. 5). The empirical formula

$$\beta=\frac{\arctan \pi DT}{1-0.4\sqrt{C}}$$

appears to give results which are in good agreement with the observed values for the yarns. The computed and observed values are plotted

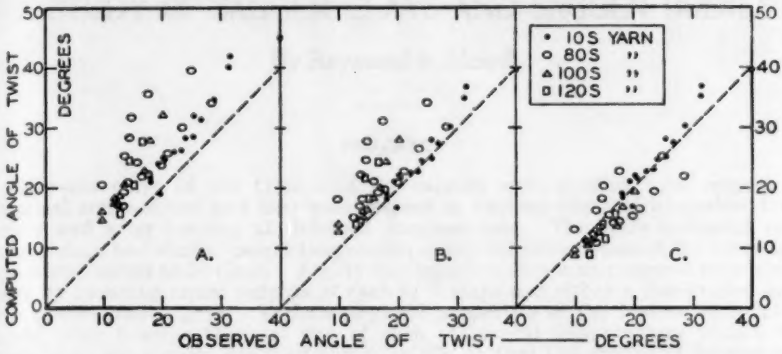

FIGURE 5.—*Relation between observed and computed values for the angle of twist.*

In A the angle of twist, β, was computed by using the formula $\tan \beta=\pi DT$.
In B the angle of twist, β, was computed by using the formula $\tan \beta=0.873\,\pi DT$.
In C the angle of twist, β, was computed by using the formula $\beta=\frac{\arctan \pi DT}{1-0.4\sqrt{C}}$.

in C of figure 5. The scattering of the points is probably attributable to the variability in the yarn and to the uncertainty in the measurements.

WASHINGTON, July 2, 1935.

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A STUDY OF SAGGER CLAYS AND SAGGER BODIES

By Raymond A. Heindl

ABSTRACT

Fifty-one clays of the type used for saggers were studied with respect to chemical composition and also with respect to various physical properties both before and after heating at different temperatures. The tests indicated that certain clays had similar properties; consequently the later phases of the investigation were limited to 36 clays. Eighty-five sagger bodies were prepared from these clays by blending equal weights of each of 2 clays and either a fine-graded grog or a coarse-graded grog. Various physical properties of the bodies were determined after heating them at one of each of several temperatures within the range in which saggers are used commercially so that 139 groups of laboratory-prepared specimens of different properties were obtained. Twelve commercially prepared bodies were also studied. The results obtained should enable the manufacturer to (1) produce saggers suitable for particular services, and (2) predict the probable life with respect to resistance to thermal shock, if certain properties of the constituent clays are known.

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I. INTRODUCTION

The practice of maturing both glazed and unglazed pottery in clay containers, or saggers as they are commonly termed, was started hundreds of years ago because of the necessity of protecting the ware from furnace gases, ashes, and rapid changes in temperature and also to make possible the stacking of the ware to heights not otherwise attainable. Saggers have received much discussion in ceramic literature because they are an important item in manufacturing costs of

various ceramic products. Not only do they break and bulge but ware is spoiled when they fail in the kiln. To assist the industry in overcoming difficulties in the use of saggers, the National Bureau of Standards undertook an extended study of a large number of clays used in sagger making and of sagger bodies prepared from those clays. Reports [1] giving in detail the results obtained have been published periodically as specific phases were completed. This paper summarizes the important conclusions reached during the course of the entire study.

Since the inception of this problem much interest has been manifested in the use of talc in sagger mixes. As a result of that interest a few tests were made to determine how the talc affected certain physical properties of the heated sagger body. The information obtained is presented as part of this report although the properties of the individual clays were not determined.

II. MATERIALS AND SCOPE OF STUDY

Among the 51 clays included in the original studies 18 were from New Jersey, 13 from Kentucky, 7 each from Ohio and Tennessee, 2 from California, and 1 each from Georgia, Illinois, Pennsylvania, and South Carolina. The samples were obtained from the consumer whenever possible rather than from the producer in order that experimental results might represent the properties of clays actually furnished to the consumer. These clays were supplemented by a limited number of commercially prepared sagger bodies.

Because of the impracticability of including all clays in every step of the investigation preliminary tests to determine such properties as pyrometric cone equivalents (softening points), strength, porosity, and linear thermal expansion, and the chemical analysis of all the clays were made in order to classify them into a limited number of groups. Representative clays from each group were chosen for further intensive study. Certain properties of these representative clays, the properties of a large number of mixtures of these clays, and the effect on certain properties such as thermal expansion, extensibility, and resistance to thermal shock, when the mixtures are heated at different temperatures, were studied.

III. PREPARATION OF SPECIMENS

Two types of bodies were used, simple and blended. The simple bodies consisted of equal parts by weight of a single clay and grog made from the same clay. The blended bodies were made in most cases from a combination of 2 clays mixed with grog made from the individual clays in each combination. All grog used with the simple bodies was heated at 1,200° C for 1½ hours before being crushed and screened. Thirty percent of this grog passed a no. 20 and was retained on a no. 40 sieve, the remaining 70 percent passed a no. 40

[1] Progress report on investigation of sagger clays. J. Am. Ceram. Soc. **9**, 131 (1926). II. Progress report on investigation of sagger clays—some observations as to the significance of their thermal expansion. J. Am. Ceram. Soc. **9**, 554 (1926). III. Progress report on investigation of sagger clays—their elasticity and transverse strength at several temperatures. J. Am. Ceram. Soc. **10**, 524 (1927). IV. Progress report on investigation of sagger clays—elasticity, transverse strength, and plastic flow at 1,000° C. J. Am. Ceram. Soc. **10**, 995 (1927). Preparation of experimental sagger bodies according to fundamental properties. BS J. Research **3**, 419 (1929) RP104; also J. Am. Ceram. Soc. **12**, 457 (1929). The life of the sagger as affected by varying certain properties. BS J. Research **7**, 1017 (1931) RP387; also J. Am. Ceram. Soc. **14**, 867 (1931). Sagger quality predicted from properties of clays used. J. Am. Ceram. Soc. **16**, 601 (1933).

sieve and included the fines. The grog for the first blended bodies investigated was prepared from clay heated at 1,230° C, but later groups of bodies contained in many cases grog prepared from the broken test specimens used in the first group. The majority of the bodies were prepared in two series similar in every respect except for the size of the graded grog, which was either coarse or fine. The two combinations of grog sizes, taken from several recommended by Kirkpatrick,[2] were as follows:

Combinations of grog	Percent	Passed through sieve no.—	Retained on sieve no.—
Coarse	20	4	8
	60	8	12
	20	12	20
Fine	66⅔	20	40
	33⅓	40	80

Test specimens, made from both simple and blended bodies, consisted of (1) bars 1 in. square in cross section and either 2, 7, or 12 in. long, and (2) small oval saggers 4 by 4 by 6 by ½ in. Some of the specimens were tested in the air-dried condition and the others had been heated for 1½ hours at one of the following temperatures (±10° C): 1,110, 1,150, 1,180, 1,200, 1,230, 1,270, or 1,300° C.

IV. METHODS OF TESTING

The water of plasticity (based on the plastic weight), the volume and linear shrinkage during drying, the porosity and the modulus of rupture of the test specimens were determined in general according to the methods adopted and later published by the American Ceramic Society.[3] The pyrometric cone equivalents (pce or softening points) were determined according to the ASTM standard method C24–20, which is similar to standard method serial designation C24–31.[4] The linear thermal expansions from room temperature to 1,000° C were measured with the apparatus described by Geller and Heindl.[5]

The relative resistance to thermal shock was determined by air-quenching empty saggers from progressively higher temperatures. The initial furnace temperature was 350° C, the second 400° C, and each succeeding temperature was increased 25° C until fracture occurred. The temperature from which they were quenched when fracture occurred is designated as T. The value of T is used as a measure of the resistance of the saggers to thermal shock.

Young's modulus of elasticity of both clays and bodies was determined with an especially designed apparatus.[6] The 1- by 1- by 12-in. bars of the mixtures of clay and grog were heated at the same time as the experimental saggers made of the same mixtures. They were then tested in flexure at several different temperatures between room temperature and 1,000° C. All elasticity tests were made using a span of 10 in.

The plastic deformation of the clays and bodies [7] was determined at 1,000° C only. The same apparatus and type of specimens were used

[2] Table 11 in Tech. Pap. BS **10**, 38 (1918) T104.
[3] J. Am. Ceram. Soc. **11**, 449 (1928).
[4] Am. Soc. for Testing Materials Book of Standards for 1930, part II, p. 184.
[5] J. Am. Ceram. Soc. **9**, 555 (1926). (See footnote 1.) A photograph of the apparatus faces p. 694, BS J. Research **3** (1929) RP114.
[6] For a description of the apparatus see J. Am. Ceram. Soc. **10**, 526 (1927), and for a photograph of it see BS J. Research **3**, 695 (1929) RP114.
[7] J. Am. Ceram. Soc. **10**, 995 (1927) and **12**, 457 (1929). See footnote 1.

for making these tests as for the modulus of elasticity tests. Measurements of the plastic flow under loads of 60 and 120 lb/in.^{2} were made at 5-minute intervals during 1 hour and similarly under a load of 30 lb/in.^{2} during ½ hour.

The total plastic deformation of the bodies was obtained from load-deflection curves. To distinguish between elastic and plastic properties the elastic recovery of the material was considered as the difference between the deflection caused by any particular load at the end of a 10-minute period and the "set" of the material at the end of a 5-minute period after removal of that load.

V. RESULTS

1. CLAYS

(a) RAW CLAYS

The water of plasticity of the 51 clays ranged from 13.7 to 31.7 percent. Forty-seven clays had satisfactory working properties.

The volume drying shrinkage ranged from 9.1 to 16.9 percent, the linear drying shrinkage from 2.8 to 6.1 percent, the porosity from 24.4 to 50.0 percent, and the modulus of rupture of dried clay bars ranged from 45 to 385 lb/in.^{2}

The pyrometric cone equivalents (pce or softening points) ranged from 14 to above 33. In this range 16 clays had a pce of 31 or above, 19 between cones 28 and 30, inclusive, 12 between cones 20 to 27, inclusive, and 4 had a pce equal to or below cone 19.

The chemical compositions of the 51 clays are given in the first progress report.[8] The silica content of 44 of the clays ranged from 50 to 70 percent, 6 contained less silica and 1 contained more. Five of the clays had an alumina content between 35 and 40 percent, 2 had less than 20 percent; the remainder ranged between 20 and 34.9 percent.

(b) HEATED CLAYS

The minimum and maximum results obtained in all tests for modulus of rupture of clays heated in the range 1,110 to 1,310° C are summarized in table 1. The detailed results (not given in this report) show that 15 clays had reached their highest transverse strength as a result of the 1,270° C heating and that 33 clays showed greater strength after having been heated at 1,310° C, although the porosity and volume shrinkage indicate the latter had been overheated at this temperature.

TABLE 1.—*Range in modulus of rupture, porosity, and volume shrinkage of 51 sagger clays heated at different temperatures*

Temperature at which heated	Modulus of rupture		Porosity		Volume shrinkage	
	Minimum	Maximum	Minimum	Maximum	Minimum	Maximum
°C	lb/in.^{2}	lb/in.^{2}	*Percent*	*Percent*	*Percent*	*Percent*
1,110	405	3,850	18.0	23.5	2.2	14.9
1,150	500	4,340	17.4	46.5	1.9	16.3
1,180	510	4,340	13.9	45.9	2.7	18.2
1,230	640	5,350	8.1	40.8	4.0	24.7
1,270	610	4,850	1.0	38.5	2.1	35.7
1,310	755	4,960	8.8	39.2	2.5	30.2

[8] J. Am. Ceram. Soc. 9, 131 (1926).

The results of the porosity and volume shrinkage determinations are also summarized in table 1. The greatest change in porosity of any clay when heated to the several temperatures given in the table was from 27.5 to 3.4 percent; the least change was from 33.5 to 31.2 percent. The greatest change in volume shrinkage was from 7.9 to 26.3 percent; the least was from 4.1 to 5.3 percent.

The linear thermal expansions of 49 clays which had been heated at 1,230° C were measured from room temperature to 1,000° C. The most distinguishing characteristic is that 34 of the clays showed a rapid increase in the rate of expansion between approximately 100 and 200° C, due to the inversion of alpha cristobalite to the beta form, while 15 failed to exhibit that phenomenon. There was a great difference (approximately 85 percent at 1,000° C) in the expansion between the clay having the greatest total expansion and the one having the least, as is illustrated in figure 1. Several additional curves for individual clays will be given later in conjunction with thermal-expansion data on sagger bodies representing mixtures of 2 or more clays and grogs.

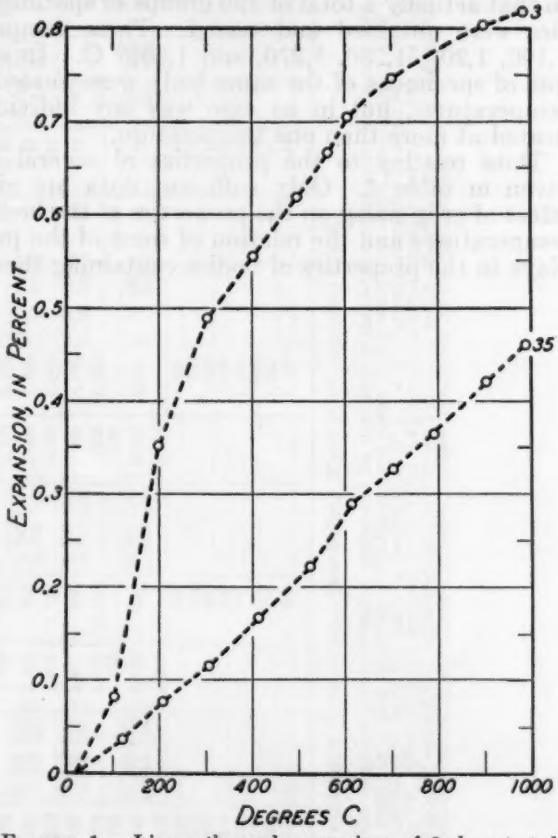

FIGURE 1.—*Linear thermal expansions of 2 clays tested after heating at 1,230°* C.
The expansions represent the extremes obtained.

The moduli of elasticity of 36 clays which had been heated at 1,230° C for 1½ hours were measured at room temperature, at 750° C, and at 1,000° C. The moduli of elasticity of the remaining 15 clays were not determined, because all types of clays included in the investigation were represented by the 36 as far as could be judged from the known properties. The modulus of elasticity at room temperature ranged from 800,000 to 9,430,000 lb/in.^{2} At 750° C the modulus ranged from 1,690,000 to 7,840,000 lb/in.^{2} The modulus at 1,000° C ranged from 300,000 to 1,510,000 lb/in.^{2}

The results of the plastic-flow tests made on 17 clays under the conditions stated, indicate that all the clays which had a pce above

30 showed little difference in the plastic flow, whereas those which had a pce of 30 or below showed not only a greater average plastic flow, but the plastic flow of the several clays in the latter group was approximately inversely proportional to the pce.

2. LABORATORY-PREPARED SAGGER BODIES

Eighty-five bodies were prepared and several of the resulting specimen bars and saggers were heated at any one of several temperatures, so that actually a total of 139 groups of specimens of different properties were obtained and tested. These temperatures were: 1,155, 1,190, 1,200, 1,230, 1,270, and 1,300° C. In some cases 3 different lots of specimens of the same body were heated at one of 3 different temperatures, but in no case was any individual lot of specimens heated at more than one temperature.

Data relating to the properties of several individual bodies are given in table 2. Only sufficient data are given to illustrate the effect of grog sizing on the properties of the bodies heated at different temperatures and the relation of some of the properties of individual clays to the properties of bodies containing these clays.

TABLE 2.—*Properties of some sagger clays and sagger bodies*

Body no.[1]	Approximate temperature of heating	Modulus of rupture R[2]			Modulus of elasticity E[2]			Total linear thermal expansion from 20 to 250° C			Extensibility R/E			Temperature sagger failure	
		Clays[3]	Fine-grogged bodies	Coarse-grogged bodies	Clays[3]	Fine-grogged bodies	Coarse-grogged bodies	Clays[3]	Fine-grogged bodies	Coarse-grogged bodies	Clays[3]	Fine-grogged bodies	Coarse-grogged bodies	Fine-grogged bodies	Coarse-grogged bodies
	°C	lb/in.²	lb/in.²	lb/in.²	1,000 lb/in.²	1,000 lb/in.²	1,000 lb/in.²	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*	°C	°C
1B	1,190		1,720	955		3,370	2,100		0.12	0.13		0.051	0.045	565	635
1B	1,230	{1,800 (21) / 1,610 (47)}	1,725	995	{3,195 (21) / 3,765 (47)}	3,800	2,305	{0.15 (21) / .11 (47)}	.11	.11	{0.056 (21) / .043 (47)}	.045	.043	540	610
1B	1,270		2,095	1,130		5,380	3,095		.11	.11		.039	.036	525	585
2A	1,230	{2,180 (24) / 2,310 (32)}	1,905	960	{2,180 (24) / 2,310 (32)}	3,605	1,525	{.13 (24) / .09 (32)}	.12	.15	.079	.053	.063	560	680
2A	1,270		2,180	1,130		4,205	2,340				.041	.052	.048	525	565
9B	1,190		1,605			2,850			.16			.056		510	
9B	1,230	{1,430 (43) / 1,395 (44)}	1,720	910	{3,395 (43) / 2,885 (44)}	3,440	2,065	{.16 (43) / .17 (44)}	.15	.16	{.042 (43) / .048 (44)}	.050	.044	485	500
9B	1,270		1,930			3,655			.16			.053		475	
2C	1,155			325			390			.10			.083		980
2C	1,270			360			615			.24			.059		585
K	1,190			595			930			.15			.064		730
K	1,230			580			1,200			.16			.045		805
K	1,270			710			1,440			.16			.049		740
M	1,190			550			920			.21			.060		475
M	1,230			715			1,265			.21			.056		490
M	1,270			755			1,620			.24			.046		415

[1] The letter following the numeral refers to the series which contained these bodies. K and M are commercial bodies.

[2] Tested at room temperature.

[3] The numbers in parentheses following the values are the identification numbers of the clays used in the bodies and are referred to in preceding reports. The average results of tests of clays may be compared with the results for similar properties of the fine-grogged bodies heated at the same temperature, namely, 1,230° C. For example, the averages for clays 21 and 47 may be compared with the values for body 1B, fine grog, heated at 1,230° C. A similar comparison may be made with clays 24 and 32 and fine-grogged body 2A; also clays 43 and 44 and fine-grogged body 9B. These examples are given to show that the properties of a body compare favorably with the properties of the clays from which prepared. The sizes of the grog in the coarse-grogged blended-clay bodies were entirely different from those used in the simple-clay bodies; consequently the results would not be in agreement. In the case of the fine-grogged blended-clay bodies and simple-clay bodies the sizes of grog were not greatly different.

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(a) LINEAR THERMAL EXPANSION

Detailed expansion data will not be given in the present paper, since they have already been published.[9] Specimens prepared from a blend of 2 clays and grog made from the same 2 clays and heated at either 1,230 or 1,270° C were classed into 3 groups, depending on whether the expansion of the body was (1) greater than that of either of the constituent clays; (2) approximately equal to the average of that of the clays; or (3) approximately equal to the clay having the lower expansion. It was also found that the bodies prepared with the coarser sizes of grog showed, in the majority of cases, a lower expansion than those prepared with the finer sizes of grog. Results indicated, as a rule, that the blended clays would be more serviceable, as judged by expansion characteristics, for making saggers than the individual clays. The linear expansion of the bodies changed with temperature of heating, but such changes were not consistent either in direction or magnitude. Figure 2 shows the linear thermal expansion of several bodies and the constituent clays.

(b) YOUNG'S MODULUS OF ELASTICITY, TRANSVERSE STRENGTH, AND EXTENSIBILITY

Young's modulus of elasticity and the modulus of rupture were determined for the heated sagger bodies at 1,000° C in the majority of cases and at room temperature, and also at some intermediate temperature in all cases. The latter temperature corresponded to that at which saggers made from any one body failed in the thermal-shock test.

The modulus of elasticity of the sagger body is in general very close to the average of that of the clays contained in the body if prepared similarly. By proper selection of clay combinations and heating temperatures it was possible to vary the modulus of elasticity in the final group of laboratory-prepared bodies from 160,000 to 4,100,000 lb/in.^{2}. The modulus of elasticity was varied also by using grog of different sizes. In all cases the bodies prepared with the coarse grog had a lower modulus of elasticity than those prepared with the fine. The difference ranged from less than 10 percent to over 170 percent, but in most cases was between 50 and 100 percent.[10]

When tested at some one temperature between 350 and 900° C, the moduli of elasticity of the bodies were, with very few exceptions, greater than the values obtained at room temperature. The increase depended mainly on the type of clays composing the individual body and the temperature at which the body was tested. Some of the bodies showed an increase of less than 10 percent; others showed considerably in excess of 100 percent.[11]

Tests made at 1,000° C showed that the moduli were in most cases greatly below the values[12] obtained at room temperature. Thus, for example, if at room temperature the modulus of elasticity was 5,000,000 lb/in.^{2}, the modulus at 1,000° C would be only about one-tenth as much; while if the initial value was 1,000,000 lb/in.^{2}, it would drop to about one-third as much at the high temperature. There is no doubt that the glassy matrix, so effective in giving a high

[9] J. Am. Ceram. Soc. **9**, 554 (1926). See footnote 1.

[10] The modulus of elasticity values from which these percentages were drawn are given in tables 2 and 3, BS J. Research **3**, 419 (1929) RP104, and table 2 BS J. Research **7**, 1017 (1931) RP387.

[11] See footnote 10.

[12] See footnote 10.

modulus of elasticity at low temperatures, contributes very little, if any, to the modulus of elasticity at 1,000° C.

The transverse strength, expressed as modulus of rupture and computed from data obtained on the same specimens used in the tests for modulus of elasticity, was affected by the initial heating temperature,

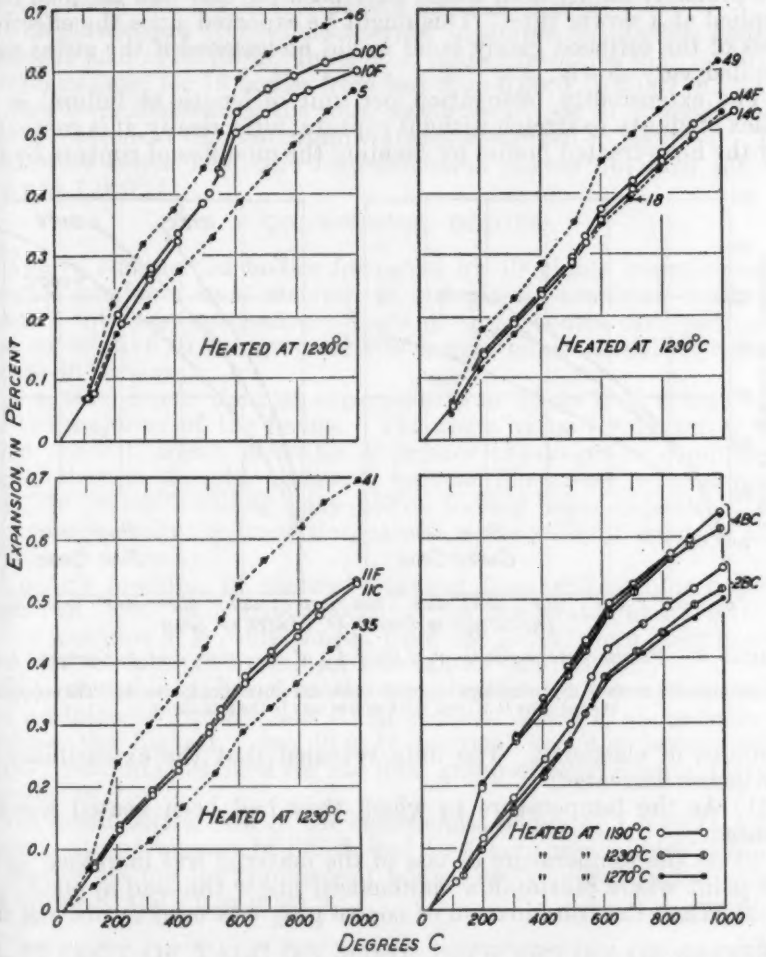

FIGURE 2.—*Linear thermal expansions of several bodies and also those of the constituent clays.*

The bodies in which comparatively fine or coarse sizes of grog were used are labeled with F and C, respectively. The curves in the lower-right portion of the figure show the expansions of 2 different bodies after having been heated at different temperatures.

grog sizing, and type of clay used in the same way as the modulus of elasticity was affected. For example, in the series of bodies in which both the type of clay and the heating temperature changed but only a combination of coarse grog was used, the modulus of rupture ranged from 120 to 2,050 lb/in.^{2} Another group of bodies selected from a series in which 3 different heating temperatures and 2 different combinations of grog sizes were used, but no change was made in the clays

of any one group, showed a range in modulus of rupture from 800 to 2,000 lb/in.[2] When tested at temperatures ranging between 350 and 1,000° C the modulus of rupture is generally greater than at room temperature. Because the tests at 1,000° C were made by rapidly increasing the load until rupture of the specimen occurred, the results are probably higher than would have been the case had the load been applied at a slower rate. This might be expected since the effectiveness of the softened glassy bond would be lessened if the stress were applied very slowly.

The extensibility (elongation per unit of length at failure) is an index of ability to stretch without rupture; numerically, it is computed for the heat-treated bodies by dividing the modulus of rupture by the

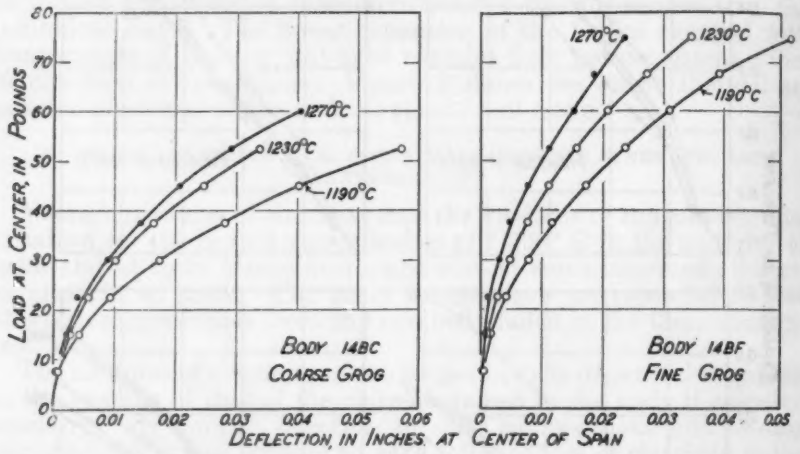

FIGURE 3.—*Plastic deformations at 1,000° C, of a coarse- and fine-grogged body.*

The temperatures at which the bodies were originally heated are adjacent to the curves. The composition of the bodies 14BC and 14BF differs only in the grog sizing.

modulus of elasticity. The data revealed that the extensibility of the bodies decreased:

(1) As the temperature to which they had been heated was increased.

(2) As the temperature of test of the material was increased up to the point where plastic flow commenced under the load applied.

(3) When the combination of coarse grog was used in place of the fine.

(c) PLASTIC FLOW

Measurements of plastic deflections were made at 1,000° C only and the results obtained, which apply only within the limits of preheating temperatures and grog sizes used, may be summarized as follows:

(1) Bodies containing the coarser sizes of grog have a decidedly greater plastic flow than those containing the finer sizes of grog.

(2) The plastic flow decreases with increase of initial heating temperature of the specimens. The data in this connection indicate the undesirability of placing heavy loads in or on saggers which have not been preheated sufficiently.

(3) The percentage increase in plastic deflection of different bodies was not proportional to the change in load when the applied load was increased 100 percent.

(4) With bodies high in flux, the plastic deflection is directly proportional to the silica-alumina ratio. On the other hand, bodies high in silica and low in flux have a low plastic flow.

The plastic flow (time-deflection) of 16 simple clay bodies under a constant load of 30 lb./in.^{2} for ½ hour ranged from less than 0.0001 to 0.0005 in., and for 18 bodies from less than 0.0001 to 0.002 in.

Six curves illustrating the total plastic deflection of 2 blended clay bodies heated at different temperatures are given in figure 3. The data were taken from the load-deflection curves obtained for the body at 1,000° C.

3. COMMERCIAL BODIES

Twelve commercial bodies furnished by 10 plants manufacturing ceramic products were received in the plastic condition ready for shaping into test specimens. Tests of these bodies divulged information relative to the properties of sagger mixes actually prepared for use in service.

The total linear thermal expansion from 20 to 250° C was high for the majority of the bodies. The mean value for 11 mixes was 0.186 percent, which indicates a greater expansion in commercial bodies than is thought necessary because laboratory tests indicate that, by proper blending, clay bodies having lower expansion, and hence more desirable properties, can be made without much, if any, additional difficulty.

Young's modulus of elasticity ranged from 665,000 for a body heated at 1,190° C to 3,160,000 lb./in.^{2} for one heated at 1,270° C.

The modulus of rupture ranged from 665 lb./in.^{2} for a body heated at 1,190° C to 1,415 lb./in.^{2} for one heated at 1,270° C.

The extensibility, based on the mean values for Young's modulus and modulus of rupture, was 0.056 percent, which is about midway between the highest value (0.0834 percent) and the lowest value (0.0277 percent) obtained for the final group of experimental laboratory bodies.[13]

The mean plastic flow of the commercial bodies at 1,000° C. when stressed at approximately 120 lb./in.^{2} for 1 hour was 0.000275 in.

The results for the commercial bodies are typified by the values for bodies K and M in table 2.

VI. EFFECT OF TALC ON SOME PROPERTIES OF SAGGER BODIES

It is not surprising that manufacturers using talc-containing sagger mixtures reported difficulties due to excessive bulging of sagger bottoms. Such bulging could readily be attributed to lowered refractoriness of the mix because talc increased the plastic flow by increasing the percentages of low-fusing glasses.

Magnesium oxide is the constituent of the talc believed to be mainly accountable for both the added good qualities of the sagger as well as those which would be considered detrimental. The brief study undertaken in this connection therefore included commercially

[13] J. Am. Ceram. Soc. 16, 601 (1933).

prepared sagger bodies containing magnesium oxide added either as talc or as magnesite. The talc was of the lime-bearing variety from northern New York, containing about 30.5 percent magnesium oxide and the magnesite was of the Grecian variety.

TABLE 3.—*Some properties of a commercial sagger body showing the effect of added talc or magnesite*

Body no.	Magnesium oxide added as—		Absorption	Pyrometric cone equivalent (pce)		Total linear thermal expansion 20° C [1] to—			Tested [2] at 20° C			Tested [2] at 625° C		Deformation [3] at 1,200° C
	Talc	Magnesite		Cone	Approx. °C	250° C	600° C	1,000° C	Modulus of rupture	Modulus of elasticity	R/E	Modulus of rupture	Modulus of elasticity	
	%	%	%			%	%	%	lb/in.²	1,000 lb/in.²		lb/in.²	1,000 lb/in.²	Inch
1	0	0	15.1	27–28	1,610	0.23	0.46	0.59	630	1,125	0.000563	750	1,435	0.0710
2	5	0	13.9	18–19	1,500	.15	.32	.46	480	556	.000858	710	1,457	.0620
3	0	5	15.0	20–23	1,550	.14	.32	.47	510	527	.000977	820	1,441	.0235
5	0	2.5	14.5	26	1,595	.18	.38	.52	470	617	.000775	790	1,345	.0230
6	2.5	0	14.2	23	1,580	.19	.39	.53	610	766	.000804	790	1,456	.0390

[1] Room temperature considered as 20° C in all tests.
[2] Average of 2 tests in all cases.
[3] Total deformation after 2½ hours at 1,200° C and a constant load of approximately 6 lb/in². The specimen (1 by 1 by 9 in.) was placed over an 8-in. span and the load was applied at midspan.

The results of all tests made are given in table 3. Although the number of test specimens was limited, the results show clearly the effects of the added talc or magnesite on the properties of the sagger body. For example, the refractoriness of the original body, as indicated by the pyrometric cone equivalent, was reduced from 1½ to 5 cones (15° to 110° C), the talc-containing bodies showing the greater change. The total linear thermal expansion was also reduced, but the reduction was approximately the same with either talc or magnesite. The extensibility of the body measured at room temperature and the plastic deformation measured at 1,200° C increased with increase in talc or magnesite content. The results show that the addition of a small percentage of magnesium oxide, either as talc or magnesite, to clay sagger bodies is beneficial both with respect to resistance to thermal shock and plastic deformation. The resistance to thermal shock may be attributed primarily to the decided reduction in the thermal expansion of the body and secondarily to the increased extensibility or stretch of the body before rupture. Any beneficial effect a small percentage of talc or magnesite may have in reducing the plastic flow is dependent on the temperature at which the saggers are used. For instance, as shown in table 3, the deformation obtained with specimens tested at 1,200° C was lower when they contained talc or magnesite than when they were free from either. When tested at 1,250° C (the data for which are not given, because of unsatisfactory end points), the 2 bodies containing talc failed because of plastic flow much sooner than the same body free from talc. The bodies containing the magnesite did not rupture during the 2½-hour test made at 1,250° C. However, in comparison with the data obtained at 1,200° C, the body containing 2.5 percent of magnesite

deformed twice as much at 1,250° C and that containing 5 percent deformed 4 times as much.

Since magnesia has such a detrimental effect on the refractoriness of clay, and this in turn is the cause of decreased resistance to plastic deformation, grog made from talc-containing saggers must be used with precaution. If the amount of magnesia in the grog is not taken into consideration when talc is added to a sagger body, it would be only a comparatively short time before the sagger mix would have little value. Actual plant records on the 2.5-percent-talc body in comparison with the talc-free body (records are not available on the other mixtures) indicated the latter had approximately one-half the service life of the former.

VII. DISCUSSION AND APPLICATION OF RESULTS TO PREDICTION OF SAGGER LIFE IN SERVICE

The two most important properties affecting the life of the sagger from the standpoint of resistance to thermal shock are believed to be thermal expansion, and extensibility or maximum strain. Since plastic flow (cause of bulging of sagger bottoms) is also an important factor in the life of saggers, it was given some study. Although conductivity is undoubtedly of some importance in connection with the resistance of clay saggers to thermal shock, no measurements of this property were made. Consequently any conclusions relative to sagger life as affected by thermal shock are based on data obtained in tests for thermal expansion, Young's modulus of elasticity, and modulus of rupture. These properties give information relative to resistance to mechanical stress (that is, modulus of rupture) and also relative to resistance to thermal shock (that is, $\frac{\text{modulus of rupture}}{\text{modulus of elasticity}}$, together with thermal expansion). In order that the manufacturer of saggers may conveniently apply the information obtained so as to produce saggers of desired quality, a chart (fig. 4) has been prepared based on those three properties determined for 73 different bodies. In this chart, T, as previously defined, is the temperature from which the sagger was quenched when fracture occurred, and is used as a measure of the resistance to thermal shock.

In the final phase of the investigation [14] a series of 12 bodies were prepared in which the information given in the chart served as a guide in predicting the service life of the saggers from the standpoint of resistance to heat shock. This was accomplished by testing the clays which it was intended to use in any one body and the approximate resistance to thermal shock was predicted by locating the mean values on the chart. Heat-shock tests were then made and the results agreed satisfactorily with the predicted life. From this it may be concluded that, if the manufacturer of saggers determines the properties of the clays after heating at the approximate temperature at which they will be used, he can readily predict the relative life of the sagger prepared from those clays by referring to the chart.

The chart shows to the manufacturer how certain important physical properties may affect the life of saggers. For instance, an examination of the left side of the figure shows that, for saggers having the same total expansion from 20 to 250° C, those having the greatest

[14] J. Am. Ceram. Soc, 16, 601 (1933).

resistance to thermal shock have both a comparatively low modulus of rupture and a low modulus of elasticity. As the lower left-hand corner is approached, both strength and modulus of elasticity increase, but unfortunately the latter increases at a much greater rate than the former. This means that the ultimate "stretch" or extensibility before rupture, is decreasing rapidly, which in turn causes the saggers to have a lower resistance to thermal shock T. The values of T, obtained by subjecting experimental saggers to thermal shock in an air-quenching test, should be considered only relative because their

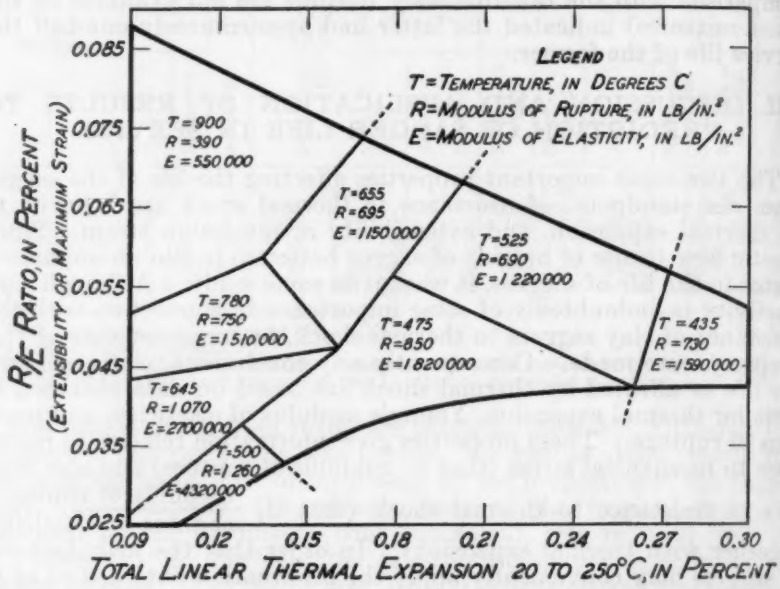

FIGURE 4.—*Areas showing the trend of the relation between resistance of saggers to failure due to thermal shock, and linear thermal expansion and extensibility.*

For all bodies included in each area are given the average values for modulus of rupture and modulus of elasticity determined at room temperature, and also the temperature T from which the saggers were quenched when fracture occurred. The trend of the values for T is considered as the trend of the resistance of sagger bodies to heat shock. The values in each area represent the mean of numerous determinations which more or less blend from one area to the adjoining ones. No sagger bodies were made which fell outside the areas bounded by the heaviest lines. The average values in the several areas for modulus of rupture and modulus of elasticity are given to illustrate that if the thermal expansion is kept constant, strength is obtained only at the expense of the extensibility because the modulus of elasticity increases at a much faster rate than the modulus of rupture.

magnitude will depend, among other things, on either the percentage or sizes of grog in the body or both and also whether the grog is vitreous or porous. As is evident from the chart, however, the determination of T by a manufacturer of saggers is not essential since the several areas always bear the same relation to one another and the location of a sagger body on the chart is determined by its R/E and thermal-expansion values, and its relative location gives an indication of its quality.

Based on our laboratory-prepared bodies it is believed that the most satisfactory sagger bodies for general purposes have the properties given in the area at the left side of the chart where T equals 780, R equals 750, and E equals 1,510,000. The modulus of rupture

of 780 is believed to be sufficient because it compares favorably with that of 12 commercial sagger bodies.

Results obtained in laboratory tests of 12 plant or commercial bodies showed 6 to have properties which placed them in the area (fig. 4) where T is 475, 3 where T is 525, and the other 3 in the area where T is 655. As far as data are available for the plant life of saggers on which laboratory tests were made they indicate that saggers having properties in the range between 0.15 to 0.18 percent for linear expansion, and 0.45 to 0.65 percent for extensibility gave the most satisfactory service. In 3 commercial plants increased life was actually obtained by shifting to the properties toward the left and top of the graph.

VIII. SUMMARY AND CONCLUSIONS

Fifty-one clays used for sagger making and representing mining districts in New Jersey, Kentucky, Ohio, Tennessee, California, Georgia, Illinois, Pennsylvania, and South Carolina were used in this investigation. A total of 85 bodies were prepared and tested in the laboratory. In these bodies 2 different series of grog sizes were used (i. e., 1 series of comparatively coarse and the other of comparatively fine sizes of grog) and 6 different heating temperatures. In addition, 17 sagger bodies used in commercial practice were tested. Two of these bodies contained talc, 2 magnesite, and another of the same clay and grog composition as the preceding 4 was free from either talc or magnesite.

The chemical compositions and pyrometric cone equivalents of the clays, and the results of such tests of the physical properties of both clays and bodies as shrinkage, porosity, modulus of rupture, Young's modulus of elasticity, linear thermal expansion, plastic deformation, and resistance to thermal shock were reported in detail in preceding reports. In this report reference is made only to extreme values.

From data obtained in the entire investigation a chart was prepared, which it is believed will permit the manufacturer of saggers to predict with a reasonable degree of accuracy the relative length of service which may be expected from saggers made from combinations of clays of which some of the properties have been determined.

Among the conclusions drawn from the results obtained the following are thought to be the most significant:

(1) Any sagger body having a total linear expansion from room temperature to 250° C of approximately 0.18 percent or greater cannot be expected to have a high resistance to thermal shock.

(2) The life of the sagger is more sensitive to changes in thermal expansion than to changes in the extensibility or "stretch" of the sagger body.

(3) There is no relation between changes in modulus of elasticity and porosity. Great increases in this molulus may accompany changes in grog sizes from coarse to fine, or higher temperatures of heating, with very little change in porosity.

(4) Bodies containing porous grog are more resistant to thermal shock than bodies containing dense or vitreous grog.

(5) Angular and loosely bonded grog particles in a body result in a high extensibility or stretch of that body, which in turn gives the body increased resistance to heat shock.

(6) The plastic deformation at 1,000° C is less in fine-grogged bodies than in coarse-grogged and decreases with increase of heating temperature. Also, the flux content is an important factor in causing plastic deformation and is more serious if the silica content is high.

(7) The addition to a sagger body of magnesia either as talc or magnesite will lead to increased sagger life, but care must be taken to control the quantity present, since both the refractoriness and plastic deformation may be affected detrimentally if too much magnesia is present.

(8) It is very desirable, and should prove profitable for the manufacturer, to analyze the conditions of service under which his saggers are to be used. In most cases it is impossible to prepare, from the ordinary sagger clays, bodies which have properties ideally suited for long life in all types of service. Therefore, by knowing certain properties of the clays and grogs available, only those suitable for his service would be used for making sagger bodies.

Acknowledgment is due R. F. Geller, under whose supervision this investigation was originally started, and M. F. Peters, B. J. Woods, W. L. Pendergast, and L. E. Mong, all of whom assisted in obtaining data at one time or another during the period of the investigation.

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EFFECTS OF FUMIGANTS ON PAPER

By Charles G. Weber, Merle B. Shaw, and E. A. Back

ABSTRACT

The National Bureau of Standards, in cooperation with the Bureau of Entomology and Plant Quarantine of the U. S. Department of Agriculture, studied the effects of commercial fumigants on papers. This was done to find which materials could be safely used to rid valuable records of destructive insects before placing the records in the new National Archives Building. A series of papers, representative of the ordinary range used in printed and written records, was treated with the following commercial fumigants known to be effective for killing insect pests: Hydrocyanic acid gas; ethylene chloride-carbon tetrachloride; carbon disulphide; ethylene oxide-carbon dioxide; methyl formate-carbon dioxide. The papers were treated with each fumigant in a chamber used by the Bureau of Entomology and Plant Quarantine for commercial-scale fumigation work. None of the fumigants had any significant deleterious effects on any of the papers, which indicated that these chemicals can be safely used for killing insect life in records of permanent value.

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I. INTRODUCTION

In the construction of the National Archives Building, every precaution was taken to provide the best possible protection for valuable Government records, but in order to insure the proper preservation of the materials stored in that depository, they must not be infested with injurious insect life when placed there. Boring insects, or the so-called "bookworms", can be eradicated by fumigation, and fumigating chambers have been installed in the Archives Building for use when necessary. A number of commercial preparations were known to be satisfactory from a standpoint of killing insect life; however no authentic information relative to the effects of any of the fumigants on paper was available. Obviously, the advantages of advanced practices for the preservation of records within the building would be lost if the fumigant used to prepare the records for storage there contributed to the deterioration of the paper. The effects of 5 fumigants on the chemical and physical properties of a series of papers representative of the types found in printed and written records were studied. The investigation was made at the request of the National Archives and with the assistance of personnel supplied by them.

II. FUMIGATION AND TESTING

The general procedure for determining the effects of the chemicals was to fumigate specimens of the papers, and determine by chemical and physical tests the resulting changes in the paper properties. The fumigating was done by the Bureau of Entomology and Plant Quarantine in a chamber used ordinarily for the fumigation of household materials. The chamber is of metal construction, gastight, and is provided with a means of exhausting the gas and rapidly changing the air within the chamber at the completion of a fumigation. The dimensions of the chamber are 10 by 8 ft 6 in.

The duration of each fumigation was 24 hr. After fumigating, all papers were allowed to season 1 week in an atmosphere of 50 percent relative humidity and 75° F, approximately the conditions that will be maintained in the Archives Building. The papers were then conditioned in the standard atmosphere at 65 percent relative humidity, 70° F before testing. The fumigants used and concentrations employed were as follows: Hydrocyanic-acid gas from 1 lb of sodium cyanide per 1,000 cu ft; ethylene chloride-carbon tetrachloride, 14 lb per 1,000 cu ft; carbon disulphide, 6 lb per 1,000 cu ft; ethylene oxide-carbon dioxide, 30 lb per 1,000 cu ft; methyl formate-carbon dioxide, 28 lb per 1,000 cu ft. At the above concentrations, all these fumigants are 100 percent effective for killing all storage insect pests[1] within 24 hr. The test specimens were suspended from cords near the ceiling of the chamber, each sheet being hung separately, with both sides exposed. The interior of the fumigation chamber and the method of exposing the paper specimens are shown in figure 1.

Eight commercial papers, 4 book papers, 3 differing as regards fiber composition and 1 with mineral coating, and 4 writing papers of different qualities were included in the study. They were tested before and after each fumigation for alpha-cellulose, copper number, acidity, and folding endurance. The alpha-cellulose content is a measure of the stable portion of the total cellulose present, while the copper number is indicative of the amount of unstable cellulose. Decrease in alpha-cellulose content, increase in copper number, and increase in acidity are all evidences of deterioration of the fibers, and the deterioration results in loss of strength, which is indicated by decrease in folding endurance. Also, both the original and the fumigated specimens were subjected to an accelerated-aging test that has been employed by the Bureau for determining the stability [2,3] of papers. This was to find whether the fumigation might have a long-range effect not immediately apparent. Since approximately 4½ months were required for completion of the fumigation study, tests on the untreated papers were repeated to find the effects of natural aging on the papers during the period of the study. Descriptions of the papers and detailed test results are given in table 1.

[1] The following U. S. Department of Agriculture articles have been issued relating to the killing of insect pests:
E. A. Back and R. T. Cotton, Farmers Bul. 1670 and 1483.
E. A. Back, R. T. Cotton, and H. D. Young, The Use of the Ethylene Oxide-Carbon Dioxide Mixture for Treating Stored Grain. Letter Circular.
E. A Back, Farmers Bul. 1353.
W. E. Hinds, Farmers Bul. 799.
I. E. Neifert, F. C. Cook, R. C. Roark, W. H. Tonkin, E. A. Back, and R. T. Cotton, Bul. 1313.
[2] R. H. Rasch and G. O. Stone, Paper Trade J. 95, T540 (July 1932).
[3] R. H. Rasch and B. W. Scribner, BS J. Research 11, 727 (1933) RP620.

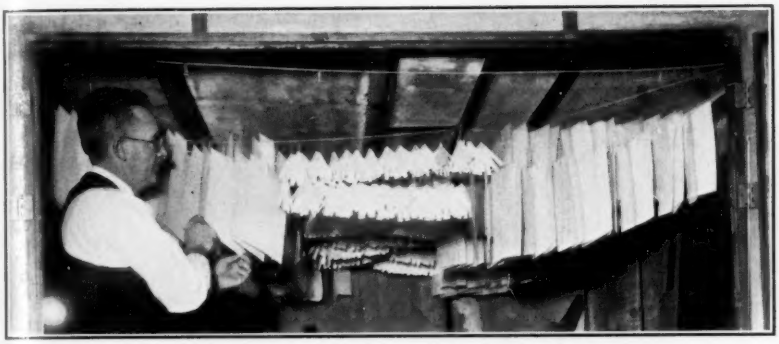

FIGURE 1.—*Fumigating chamber with specimens in place for exposure.*
The strips are for folding endurance tests and the sheets for chemical tests.

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TABLE 1.—*Effects of fumigants on properties of eight papers*

[Folding-test results marked * were obtained with the MIT tester at .5-kg tension; all other tests were made by the methods of the Technical Association of the Pulp and Paper Industry]

Papers				Chemical tests				Heated 72 hours at 100° C		
				Acidity						
Number	Description	Fumigant used	Folding endurance (avg both directions)	By Kohler-Hall method	pH of extract (quinhydrone electrode)	Alpha-cellulose	Copper number	Retention of folding endurance	Decrease in percentage of alpha-cellulose content	Increase in copper number
			Double folds	*Percent*	pH	*Percent*		*Percent*		
1	Machine-finish; book; soda-sulphite; weight 25×38:500 50 pounds.	None (original paper)	* 155	0.054	5.86	80.25	3.00	81	2.25	0.10
		Hydrocyanic-acid gas	* 141	.032	5.80	80.42	3.09	90	1.97	.35
		Ethylene chloride-carbon tetrachloride	* 176	.032	5.85	80.02	3.09	77	1.20	.31
		Carbon disulphide	* 165	.020	5.87	80.21	2.97	66	1.67	.47
		Ethylene oxide-carbon dioxide	* 161	.008	5.80	80.09	3.03	73	2.21	.43
		Methyl formate-carbon dioxide	* 145	.011	5.80	80.49	3.03	72	3.09	.49
		None (original after 4½ months)	* 168	.020	5.70	79.75	3.08	80	2.37	.15
2	Single-coated book; soda-sulphite; weight 25×38:500 70 pounds.	None (original paper)	* 803	.024	7.60	69.69	3.81	70	0.00	.02
		Hydrocyanic-acid gas	* 849	.002	7.55	72.77	3.97	60	2.72	.11
		Ethylene chloride-carbon tetrachloride	* 840	.002	7.63	73.14	3.66	62	5.37	.30
		Carbon disulphide	* 678	.006	7.60	71.11	3.76	92	1.44	.41
		Ethylene oxide-carbon dioxide	* 755	.006	7.68	71.35	3.83	62	1.67	.12
		Methyl formate-carbon dioxide	* 831	.007	7.65	71.23	3.89	85	3.84	.10
		None (original after 4½ months)	* 877	.004	7.60	71.28	3.45	67	1.93	.93
3	Machine-finish; book; 50-percent rag; weight 25×38:500 40 pounds.	None (original paper)	* 161	.078	4.68	85.51	2.34	81	2.47	.36
		Hydrocyanic-acid gas	* 146	.080	4.70	85.36	2.36	100	3.15	.34
		Ethylene chloride-carbon tetrachloride	* 160	.068	4.82	83.18	2.64	79	2.12	.17
		Carbon disulphide	* 126	.077	4.65	84.53	2.68	100	2.14	.28
		Ethylene oxide-carbon dioxide	* 162	.046	4.95	84.71	2.47	73	2.47	.25
		Methyl formate-carbon dioxide	* 142	.063	4.76	84.78	2.48	96	4.76	.44
		None (original after 4½ months)	* 186	.054	4.90	84.58	2.60	80	1.92	.07
4	Machine-finish; book; 100-percent rag (new); weight 25×38:500 45 pounds.	None (original paper)	1,696	.020	5.64	97.78	.53	84	2.37	.22
		Hydrocyanic-acid gas	1,445	.027	5.40	97.50	.54	100	2.12	.28
		Ethylene chloride-carbon tetrachloride	1,419	.018	5.45	96.77	.60	100	1.57	.27
		Carbon disulphide	1,617	.018	5.55	97.30	.67	87	1.78	.12
		Ethylene oxide-carbon dioxide	1,541	.013	5.45	97.04	.50	81	1.44	.10
		Methyl formate-carbon dioxide	1,349	.015	5.40	96.91	.54	92	1.41	.24
		None (original after 4½ months)	1,426	.017	5.35	97.20	.60	83	1.98	.22

TABLE 1.—*Effects of fumigants on properties of eight papers*—Continued

Papers		Fumigants used	Folding endurance (avg both directions)	Chemical tests				Heated 72 hours at 100° C		
				Acidity		Alpha-cellulose	Copper number	Retention of folding endurance	Decrease in percentage of alpha-cellulose content	Increase in copper number
Number	Description			By Kohler-Hall method	pH of extract (quinhydrone electrode)					
			Double folds	*Percent*	pH	*Percent*		*Percent*		
5	Sulphite bond; weight 17×22:500 20 pounds; starch surface sizing.	None (original paper)	167	0.064	4.50	79.83	3.02	23	1.91	0.53
		Hydrocyanic-acid gas	159	.077	4.60	80.09	3.04	17	3.64	.46
		Ethylene chloride-carbon tetrachloride	168	.063	4.56	79.98	3.34	21	4.47	.19
		Carbon disulphide	117	.069	4.50	78.77	3.31	22	1.94	.43
		Ethylene oxide-carbon dioxide	128	.042	4.74	79.36	2.99	27	3.67	.44
		Methyl formate-carbon dioxide	111	.061	4.70	78.55	3.28	19	1.05	.32
		None (original after 4½ months)	127	.060	4.55	78.82	3.19	16	2.99	.59
6	25-percent-rag bond; weight 17×22:500 20 pounds; starch surface sizing.	None (original paper)	650	.023	5.12	89.02	2.01	62	1.22	.47
		Hydrocyanic-acid gas	644	.037	5.16	89.30	2.04	57	2.41	.38
		Ethylene chloride-carbon tetrachloride	661	.023	5.05	88.64	2.11	61	.91	.40
		Carbon disulphide	518	.027	5.06	88.70	2.10	69	.89	.47
		Ethylene oxide-carbon dioxide	567	.036	5.22	88.71	2.12	62	1.56	.49
		Methyl formate-carbon dioxide	601	.026	5.25	88.52	2.22	57	1.08	.34
		None (original after 4½ months)	548	.026	5.05	88.62	2.18	57	1.57	.48
7	50-percent-rag bond; weight 17×22:500 20 pounds; starch surface sizing.	None (original paper)	564	.031	5.07	88.86	1.38	68	1.42	.46
		Hydrocyanic-acid gas	496	.056	5.05	88.94	1.39	64	2.58	.40
		Ethylene chloride-carbon tetrachloride	521	.022	5.22	87.67	1.42	60	1.27	.42
		Carbon disulphide	508	.038	5.13	88.13	1.38	67	1.74	.37
		Ethylene oxide-carbon dioxide	428	.030	5.18	87.73	1.32	65	1.26	.33
		Methyl formate-carbon dioxide	447	.035	5.30	87.80	1.40	62	.81	.50
		None (original after 4½ months)	445	.037	5.10	88.34	1.44	69	1.04	.43
8	100-percent-rag bond; weight 17×22:500 20 pounds: glue surface sizing.	None (original paper)	3,309	.031	5.62	97.82	.98	72	.94	.14
		Hydrocyanic-acid gas	3,008	.047	5.30	98.00	.70	71	.80	.54
		Ethylene chloride-carbon tetrachloride	2,968	.036	5.46	97.16	.84	77	.30	.25
		Carbon disulphide	2,829	.032	5.47	97.34	.76	73	.59	.30
		Ethylene oxide-carbon dioxide	2,822	.022	5.68	97.18	.86	78	.55	.10
		Methyl formate-carbon dioxide	2,612	.033	5.55	97.45	.86	75	.42	.16
		None (original after 4½ months)	2,706	.029	5.50	97.70	.94	68	.61	.21

III. DISCUSSION OF RESULTS

The results given in table 1 show the strength, chemical properties, and stability of each paper before fumigating; after fumigating with each gas; and after 4½ months of natural aging without fumigating. Decreased alpha-cellulose content, increased copper number, increased acidity, or loss of folding endurance after fumigation, would be indicative of harmful effects. However, the properties are related and a deteriorative effect serious enough to change one property would be expected to change one or more of the others correspondingly. Hence, changes in single properties could not be considered conclusive unless excessive.

None of the fumigants had any marked deteriorative effects on the papers. Papers 2 and 3 apparently showed some loss of folding endurance from carbon disulphide; however, in neither instance was the loss of strength accompanied by corresponding changes in the chemical properties, or loss of stability as indicated by the heat test. Some irregularity in the values for alpha-cellulose and copper number for papers 2, 3, and 5 may result from effects of the fumigants; however, no definite trend to indicate deleterious action of any fumigant is in evidence. In most instances, tests made before and after fumigating checked as well as the tests on the untreated papers before and after 4½ months of natural aging. From a consideration of these data, it appears that none of the 5 fumigants used had any significant effects on the properties or stability of any of the papers.

IV. SUMMARY AND CONCLUSIONS

Normal fumigation with hydrocyanic acid gas, ethylene chloride-carbon tetrachloride, carbon disulphide, ethylene oxide-carbon dioxide, or methyl formate-carbon dioxide had no significant effects on representative book and writing papers. The results indicate that these effective fumigants, all of which are commercially available, can be safely used for ridding valuable documents and books of destructive insects, a step often necessary in preparing material for preservation in modern depositories.

The assistance of M. J. O'Leary, E. E. Creitz, J. E. Gibson, and M. Reiss in the laboratory testing is gratefully acknowledged.

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U. S. Department of Commerce National Bureau of Standards

RESEARCH PAPER RP829

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ACCURACY OF MICROSCOPICAL METHODS FOR DETERMINING REFRACTIVE INDEX BY IMMERSION

By Charles Proffer Saylor

ABSTRACT

The accuracy of the immersion methods used in petrography for determining refractive indices is limited by the sensitivity of the criterion of match. In a series of tests, the sensitivity of three methods of ascertaining match was investigated as a function of objective aperture and size and shape of particle. The following data will illustrate the way in which experimental details, represented in the literature as equally good, can influence the accuracy of a result. A single determination of the refractive index of potassium alum has a probable error originating in the criterion of match which is as small as 0.00008 when the double-diaphragm method and an objective, 3.2×, N.A. 0.11, are employed, or as large as 0.00104 with central illumination and an objective, 45×, N.A. 0.85. The similar error with potassium chloride ranges between 0.00014 and 0.00125, depending upon conditions. All methods are more sensitive with objectives of low numerical aperture.

The magnitude of the errors introduced by birefringence was studied by tests of a strongly birefringent compound under a broad variety of conditions. To show the influence of conditions upon accuracy, two examples may be cited. Employing a 20×, N.A. 0.40 objective, plane polarized light with its vibration parallel to the horizontal crosshair, and ordinary oblique illumination from the side, the error in determining the extraordinary refractive index of mercuric cyanide is +0.0056, but employing a 10×, N.A. 0.25 objective, light with its vibration parallel to the horizontal crosshair, and double-diaphragm illumination, oblique from the side, the error is less than 0.0001.

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I. SENSITIVITY OF THE CRITERION OF MATCH

1. INTRODUCTION

Determination of refractive index by immersion is probably the most important operation in the microscopical identification of crystalline compounds. Crystals or crystal fragments are mounted in a liquid of known index. One of several criteria for indicating qualita-

tively the relation between the indices of the crystals and the liquid is employed and the properties of the liquid are modified accordingly until, after repeated trials, a liquid is found whose refractive index matches that of the particle. In work of the highest precision, monochromatic, plane polarized light with its vibration parallel to a principal optical direction of the crystal is employed, and the efforts at matching are continued until it cannot be ascertained that the index of the crystal differs from that of the liquid.

The sensitivity of the criterion of match limits the ultimate attainable accuracy of such determinations. Other factors can, with patience, be controlled to such degree that the errors they create are small. But there is confusion and disagreement in the literature concerning the relative sensitivity of various methods of testing for a match in index. The following quotations from three of the most authoritative works in English will illustrate this situation.

> Under the same conditions, the accuracy of the Becke line method and of the oblique illumination method is about the same when applied to mineral grains immersed in refractive liquids. With monochromatic illumination (strong sodium light) the refractive index of an isotropic clear mineral grain can be determined with an accuracy of ± 0.001, even though the diameter of the grains is only 0.01 to 0.02 mm. * * * in the Becke line method a higher power objective is advisable, the substage diafram must be closed or the condenser lowered, and practically only one mineral grain can be tested at a time. (F. E. Wright, The Methods of Petrographic-Microscopic Research, p. 96, Carnegie Inst. Washington Pub. 158, Washington, D. C., 1911.)

> This bright line is the "Becke line"; it moves toward the mineral of higher index when the focus is very slightly raised. The plane of contact should be normal or nearly normal to the plane of the section for the best results. * * * By the use of oblique illumination the same phenomenon may be made more distinct, so that differences of index as small as 0.001 may be detected promptly under favorable conditions. (A. N. Winchell, The Microscopic Characters of Artificial Inorganic Solid Substances or Artificial Minerals, p. 59, John Wiley and Sons, Inc., New York, 1931.)

> The Becke line may be used also with the immersion method. It is more sensitive and easier to see than the light and dark borders produced by inclined illumination and at the same time it may be seen over the whole field of the microscope at once. * * * A series of tests by de Lorenzo and Riva show it to be accurate to ± 0.001. (Albert Johannsen, Manual of Petrographic Methods, 2d ed. p. 277, McGraw-Hill Book Co., New York, 1918.)

No one appears to have made a critical study of the actual sensitivity of immersion methods since that of G. de Lorenzo and C. Riva.[1] They used only the method of central illumination (at least in the place indicated) and do not say what objectives were used. Nevertheless, their statements seem to be the origin of the almost occult number, 0.001, which recurs in subsequent literature for the accuracy of refractive-index determinations.

If the identification of substances by a measurement of their refractive indices by immersion is to find its fullest usefulness in chemical analysis, the accuracy with which the refractive indices can be found should be not appreciably less than the reproducibility of the compounds themselves. It is unfortunate that the attainable accuracy should be unknown or lost in the confusion of conflicting opinions. With the hope of limiting so far as possible the uncertainty originating in the criterion of match, experiments were undertaken to learn the real sensitivity under various conditions of the method of central

[1] Atti Accad. Sci. Napoli [2] **10**, no. 8, 9 (1901). They refer to an earlier paper by one of them in the words, "Uno di noi in una prossima nota avrà occasione di indicare l'approssimazione, che con questo metodo si può ottenere, e i vantaggi che esso presenta per la determinazione dei minerali che compongono le rocce". No indications are given of where the earlier paper was published and I have not found it.

illumination (Becke line), the method of oblique illumination, and a modification of the oblique-illumination method which, for brevity, can be called the double-diaphragm method. After preliminary experiments, each of these methods was employed in the manner which permitted it to reach the greatest sensitivity for any substance and magnification. For the highest sensitivity (and accuracy), an intense source of monochromatic light must be employed, and, if the test substance is birefringent, the light vector must vibrate parallel to a principal optical direction of the substance.

2. METHOD OF CENTRAL ILLUMINATION

In the method of central illumination, fragments of a material are mounted in the liquid with which its index is to be compared and viewed by a symmetrical cone of light focused, for the best results, approximately in the plane of the preparation. This point is often neglected on the erroneous assumption that a strictly parallel beam, though unattainable, is theoretically the most desirable condition. It is necessary that the angle of the cone be considerably less than the angular aperture of the objective, but the precise ratio depends upon the conditions of the particular experiment. When the objective is elevated from the position of truest focus, a bright line or zone appears and moves from the interface between the material and the immersion fluid toward the medium of higher index. If the objective is lowered, the reverse effect occurs. When, for light of a single wave length, the index of the liquid is made to match that of the material, the bright line disappears and the outline of the fragment vanishes.

Among other things, the sensitivity of the method depends upon the shape and size of the fragment, the angle of the cone of light, its luminous intensity, and the numerical aperture [2] of the objective.

3. METHOD OF OBLIQUE ILLUMINATION

When viewed by oblique illumination, a fragment mounted in a liquid of lower index appears (by inversion in the microscope) to be bright on the side from which the light actually comes, and shaded on the opposite side. If the fragment is mounted in a liquid of higher index, the conditions are reversed. At least nine methods for obtaining oblique illumination have been described, seven being listed by Wright.[3] The best, in the most perfect form that is ever really used, is as follows. The light source, or a condensing lens placed before it, is sharply focused by the condenser in the plane of the preparation. The iris diaphragm of the condenser is so adjusted that the condenser aperture is a little greater than that of the objective. The ocular is removed or the Bertrand lens is focused upon the back element of the objective. An opaque stop, the end of a celluloid ruler, for example, is inserted in the condenser system at such a level that a sharp image of it is formed at the back surface of the objective. It is pushed across until about a fifth of the diameter of the back surface of the objective is still bright. Then, if the Bertrand lens is removed or the ocular replaced,

[2] Concerning numerical aperture it should be noted that in each of the places cited a high numerical aperture or, what is equivalent to it, a high-power objective, has been recommended for Becke line effects as yielding greater sensitivity, but that such conclusions are not confirmed by the experiments here reported (see figs. 5, 6, 7, 8, 9, and 10).

[3] F. E. Wright, Am. J. Sci. 185, 63 (1913).

the entire field of the microscope is seen to be dimly but uniformly lighted. The objective mounting, by serving as a second diaphragm, intercepts about half of the light from the stage. Since the opaque stop in the condenser has been made approximately conjugate with the objective mounting, both the rays which are intercepted and those which pass through come uniformly from all parts of the field. Optical inhomogeneities in the field change the path of the rays, and relatively small angular deviations may cause them to fall on a different side of the boundary imposed by the objective mounting. From the chosen point A, figure 1, rays diverge and spread to every part of the field, but unless their paths are changed by the preparation all are stopped by some part of the objective mounting. If the index of the liquid is greater than that of the crystal, the ray which strikes the left side of the crystal in figure 1, is deflected to the left and caused to fall within the aperture of the objective. Thus the left side of the crystal (apparently the right side) is made brighter. Rays from point B, on the other hand, pass into the objective and serve to illuminate all parts of the field unless, as by striking the right edge of the crystal, they are so deflected as to be intercepted by the objective mounting. In such manner originate the bright and shaded portions of particles immersed in a fluid of different index.

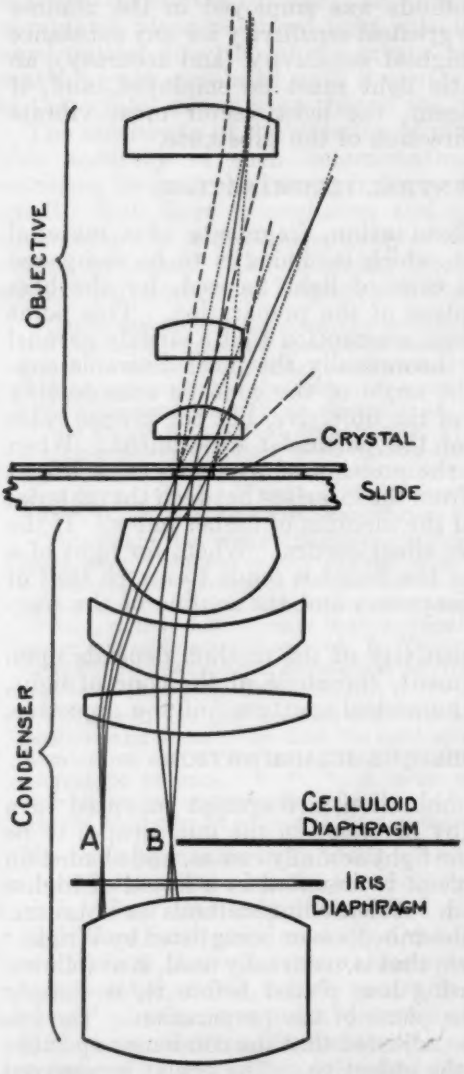

FIGURE 1.—*Oblique illumination.*

Condenser, diaphragms, preparation, objective, and ray paths. The rays, drawn as full lines before they reach the preparation, are refracted if they strike the edges of the crystal. The courses they then take are drawn as dashed lines and the courses they would have taken if not deflected are shown as dotted lines. Some rays, striking such parts of the preparation that they are not appreciably deflected, have been continued through as full lines. The index of the crystal is assumed lower than that of the liquid.

Both theoretically and practically, the best setting of the opaque stop in the condenser is the one described above, in which it is at such a level that no part of the field is darkened more than any other. Its advantage is that all light reaching any part of the field comes along

a chosen path. With the diaphragm at any other level, the oblique light reaching any part of the preparation is always mixed with light from other directions, with an uncertain amount of directly transmitted light, and even with light coming obliquely from the opposite direction. This tends to obscure the evidences of heterogeneity.

The sensitivity of the method is influenced by the size and shape of particles, the numerical aperture of the objective, the brightness of the light, the diaphragm settings, and by the perfection of corrections in the marginal zones of the objective, since these alone serve for the formation of images.

4. DOUBLE-DIAPHRAGM METHOD OF OBLIQUE ILLUMINATION

In section 3 the ordinary method of oblique illumination was explained by considering the mounting of the objective as a second diaphragm which intercepts most of the undeviated light from the condenser. It is a logical extension from this to increase the sensitivity by placing another diaphragm at the objective in a position which is deliberately chosen to give the best results. Wright [4] described a method in which two diaphragms were used, but since one was placed below the polarizer and the other between the objective and the slide, they formed diffuse images in the field of vision. Only a band at the center could be successfully employed and the method appears to have fallen into disuse.

The double-diaphragm method which has been tested is a modification of the foregoing. A piece is cut from a thin filing card in the form:

This is laid upon the back element of the objective so as to block the right half of the objective aperture. The edge of a piece of sheet aluminum or the end of a celluloid ruler is pushed into the condenser system from the right. Its image at the back of the objective appears from the left. It is adjusted vertically so as to form an image in the plane of the cardboard piece resting on the back element of the objective. When the entire field of the microscope is dimly but uniformly lighted, the diaphragm in the condenser is clamped in position. By removing the ocular, the back of the objective is seen as follows:

From the chosen point A, figure 2, rays spread to every part of the field, but unless their paths are changed by the preparation all are intercepted by the special diaphragm in the objective. The crystal, however, has a different index of refraction than the fluid and that ray which strikes it on its left edge is deflected and caused to fall within the unobscured portion of the objective aperture. Rays from the point B, on the other hand, passing through the objective serve to illuminate all parts of the field unless portions of the crystal—the right edge—deflect them so that they are stopped by the special diaphragm. When a test is being performed and a particle has been made nearly invisible, the iris diaphragm and the mask in the condenser are adjusted to such positions that the light and dark shadings

[4] J. Wash. Acad. Sci. 4, 389 (1914).

of the particle have a maximum distinctness. This setting does not as a rule need to be changed so long as the same objective is employed.

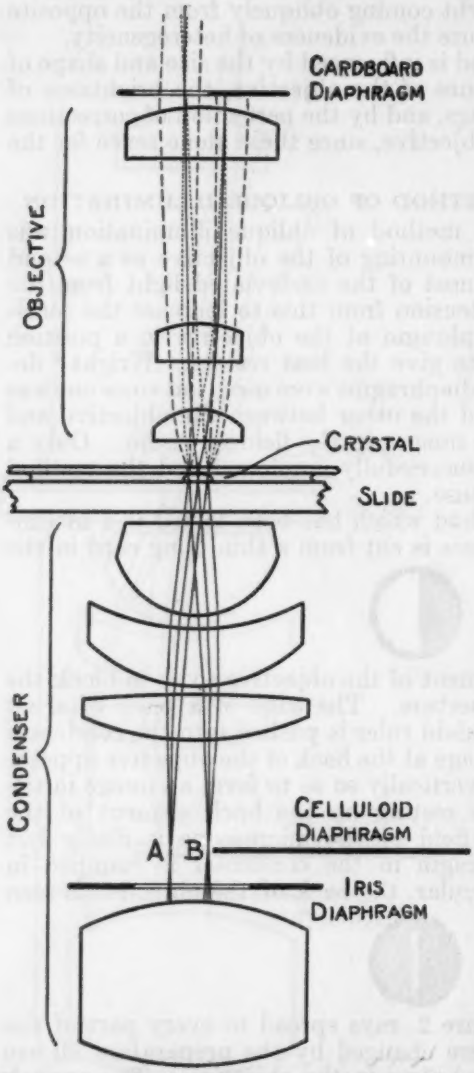

FIGURE 2.—*Double-diaphragm method of oblique illumination.*

Condenser, preparation, objective, iris diaphragm, special diaphragms in condenser and objective, and ray paths. The rays, drawn as full lines before they reach the preparation, are refracted if they strike the edges of the crystal. The courses they then take are drawn as dashed lines and the courses they would have taken if not deflected are shown as dotted lines. Some rays, striking such parts of the preparation that they are not appreciably deflected, have been continued through as full lines. The index of the crystal is lower than that of the liquid.

The double-diaphragm method of oblique illumination has been tried, in the form described above, with five types of petrographic microscopes that were accessible to the author. There were differences in ease of manipulation, but a critical placing of the two diaphragms was possible with all of them.

The sensitivity of this method also is dependent, among other things, upon numerical aperture, size and shape of particle, correctness of diaphragm settings, and brightness of light.

5. TEST SUBSTANCES

The sensitivity of these methods was tested practically by using four substances, selected because of their shapes and the values of their refractive indices. Potassium chloride grown directly upon the slide has no inclined faces, the vertical interfaces between crystal and liquid being the only ones by which failure of crystal and liquid to match can be observed. Potassium alum, grown upon the slide, has no vertical surfaces, and the octahedron faces inclined 19°28′26″ from vertical provide all useful refraction effects. Particles of crushed borosilicate laboratory glass have irregular surfaces and resemble in configuration the powders on which petrographic determinations are usually made. Glass wool was chosen because it has no angular edges and because its refraction effects are similar to those of spheres. During tests, all substances but the crushed glass were so oriented that refracting surfaces were normal to the plane of incidence.

6. APPARATUS AND TEST PROCEDURE

The general scheme of the tests was that of observing one particle immersed between slide and cover glass in a known liquid and then, using each of the three methods for determining match, the conditions were so modified that the index of the particle repeatedly became just detectably higher and then just detectably lower than the index of the liquid. To avoid spurious effects, a setting was considered for recording only when two opposite sides of the particle were faintly visible and indicated the same relation between the indices of the particle, and the immersion liquid.

Gaubert's [5] plan of varying the temperature to adjust the index of an immersion liquid with respect to a particle was adopted. Since the temperature coefficient of refractive index is from 3 to 1,000 times as great for liquids as for crystals having about the same index, such adjustments are usually possible with a liquid of suitable index. In the present study, mounts were made upon a special slide or cell, [6] with which temperature control is secured by running a rapid stream of water between microscope cover glasses. This device, which has about the same optical thickness as an ordinary microscope slide, allows the entire illuminating cone of the condenser to be employed when desired and permits normal relationships between condenser, preparation, and objective. In consequence, the apparatus for controlling temperature imposed no modification upon any method of determining match. The temperature of the water circulating through the slide was regulated by means of a valve which adjusted the proportions of hot to cold water. The hot and cold water were drawn from overflow tanks, suspended from the wall, through which the ordinary tap water of the building was circulated. Thus by the shifting of a single calibrated lever, the temperature of a liquid in which particles were mounted could be precisely regulated between 15 and 50° C. One-tenth of a degree corresponded to about 0.7 mm on the graduated dial.

The immersion liquids were chosen, so far as possible, from a series of complex esters [7] of extraordinary stability. Potassium chloride crystals were mounted in bisethoxyethyleneglycol phthalate. For potassium alum and the crushed borosilicate glass, appropriate mixtures of bisethoxydiethyleneglycol adipate and bisbutoxyethyleneglycol phthalate were employed. These liquids were thoroughly stable and did not suffer change in index, so far as could be detected, after several days at temperatures fluctuating between 25 and 40° C. For glass wool, no fully satisfactory liquid seemed to be available. The mixture of mineral oil and monochloronaphthalene which the writer uses as an index liquid of 1.520 was employed, but by the loss of the monochloronaphthalene its index slowly became lower during use. The results with the glass wool are given, therefore, not in terms of relative refractive index, but as deviations from a mean value (see figure 6). For a series of temperatures between 20 and 40° C, the index of each liquid was determined upon a special, low-reading, Abbe refractometer [8] with which, by applying a correction, it is possible to obtain results accurate within 2 or 3 units in the fifth decimal place.

[5] Bul. soc. franç. minéral. 45, 89 (1923).
[6] C. P. Saylor, J. Research NBS 15, 97 (1935) RP814.
[7] These compounds were synthesized by C. H. Binkley, to whom the writer is much indebted.
[8] Warren P. Valentine, Philadelphia, Abbe refractometer 368.

In all tests, temperatures were determined by means of a 5-junction, copper-constantan thermocouple, with its warm end placed between the slide and cover glass so that it was just at the edge of the field when the 45× objective was used. The thermocouple wire was no. 38 AWG. Junctions were electrically welded and filed at the welds to remove all excess metal. They were arranged so that the tips were in one straight line and the wires all in the same plane. They were held in this position by an insulator 1 cm back from the tips so that it was well outside the cover glass. The thermocouple caused a separation of about 0.1 mm between slide and cover glass. A bath of shaved manufactured ice and previously chilled distilled water in a vacuum flask served to maintain the cold junction. All readings were made with the same potentiometer as had been employed in calibrating the thermocouple itself.

Four different objectives were used: no. 1, 3.2×, N.A. 0.11; no. 3, 10×, N.A. 0.25; no. 4, 20×, N.A. 0.45; and no. 6, 45×, N.A. 0.85. The same 10× ocular was used throughout. All tests were made with the filtered 577 and 579mμ lines of the mercury vapor arc. The laboratory was not darkened during any of the tests although the microscope stage was shaded whenever desirable.

The most critical point was that of determining the temperature corresponding to the least detectable difference in index between a particle and the immersion liquid. When a temperature was found at which the index difference was small but still readily perceptible, the conditions were adjusted in every detail to make the evidences of failure to match as conspicuous as possible. This setting, once made for a given preparation, objective, and method, was maintained for all tests. It was checked, however, at the completion of a run after the attainable sensitivity was known. Then the temperature was adjusted upward and downward to obtain a series of readings. A temperature setting was made which was lower than the conditions producing invisibility. As this temperature was slowly raised, the contrast between the particle and the liquid diminished. When the least perceptible gradations on opposite sides of the particle showed that its index was lower than that of the liquid, the potentiometer was read, but to guard against changes while the potentiometer was being set the appearance of the field was checked before making a record. A similar reading was made for conditions where the index of the particle was higher than that of the liquid. Thus a series of readings was obtained for each objective, substance, and method, there being as a rule five readings when the index of the liquid was above and five when it was below that of the chosen grain.

7. DATA AND THEIR SIGNIFICANCE

Figure 3 for potassium chloride, figure 4 for alum, figure 5 for crushed glass, and figure 6 for glass wool give the results of tests. Opposite the designation of each objective are plotted all the index determinations made with it. The determinations by each method are arranged in columns. A plus sign indicates that the index of the liquid can be seen to be higher than that of the particle, and a minus sign that the index of the liquid is lower than that of the particle. In each section, the points are arranged from left to right in the order of observation. The vertical distance between the rows

of plus and minus signs is a measure of the uncertainty of any single determination. From the data several conclusions are possible.

(a) Under similar conditions, the double-diaphragm method is more sensitive than either of the others.

(b) The ordinary method of oblique illumination is usually the least sensitive. In two cases out of ten the method of oblique illumination

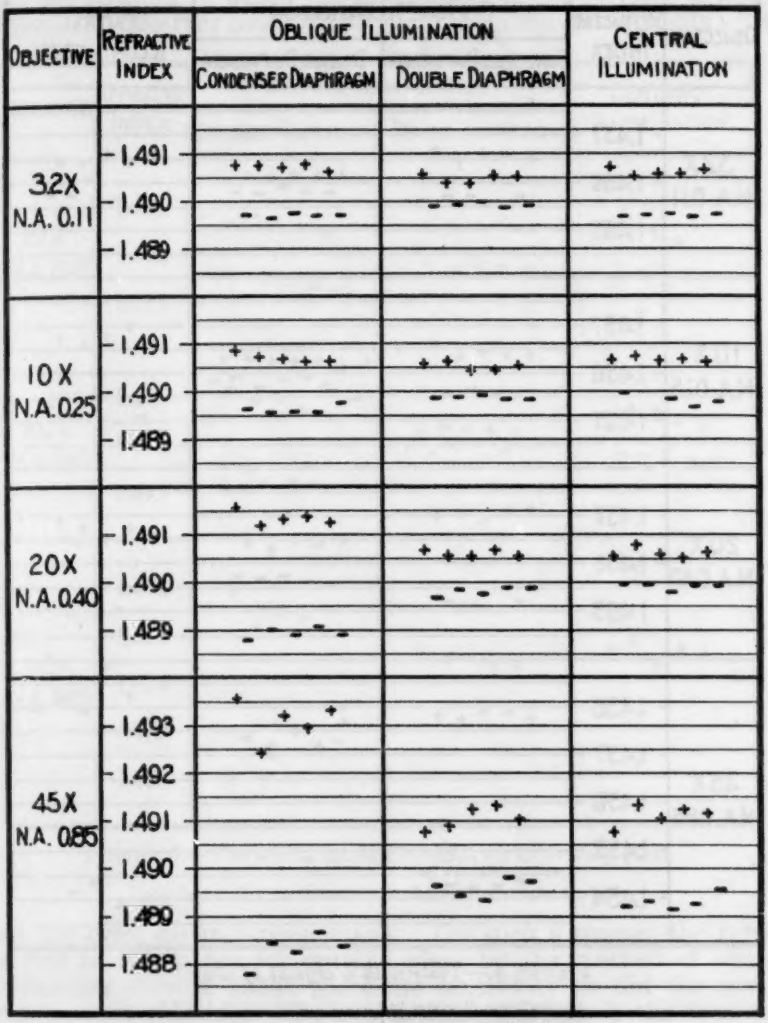

FIGURE 3.—*Tests with a crystal of potassium chloride.*

Approximate diameter 65μ.
Mean temperature 38.88° C.
From International Critical Tables, $n_{\frac{38.88}{578}} = 1.49034$

seems to be slightly more sensitive than the method of central illumination, but the difference is about the same as the uncertainty of the tests.

(c) By all methods, low-power objectives give greater sensitivity than high-power objectives. For the method of central illumination,

this is unsupported by most of the literature,[9] but it is a theoretical necessity. The immersion methods are all deviation methods. In general, a particle immersed in a liquid deflects a certain part of the light rays which strike it, but as the difference in index between a particle and its environment becomes progressively smaller, the

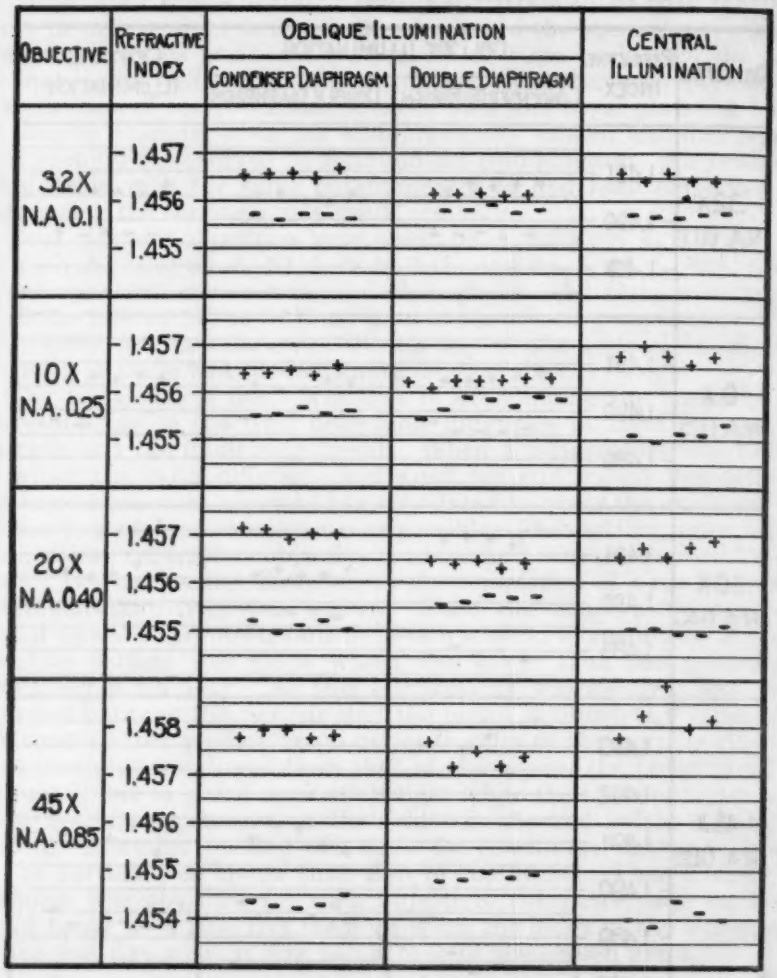

FIGURE 4.—*Tests with a crystal of alum.*

Approximate diameter 74μ.
Mean temperature 30.25° C.
From International Critical Tables, $n_{\frac{30.25}{D}}^{\frac{30.25}{5461}} = 1.45618$.

extreme angular deviation decreases until the effect can no longer be detected. A given angular deviation is a smaller part of the angular aperture of a high-power objective than of a low-power one, hence a small difference in index with a low-power objective is equivalent to a larger difference with an objective of higher power.

[9] E. M. Chamot and C. W. Mason, Handbook of Chemical Microscopy, vol. I, p. 309, John Wiley and Sons, New York, 1930, correctly recommend an objective of low aperture.

(d) The method of central illumination is subject to relatively large differences, depending upon the shape of a particle. The sensitivity is about twice as great with a substance like potassium chloride (vertical surfaces) as with alum (inclined faces). Unless the surface lies within the cone of illumination so that light can approach from both sides, there is a great loss of sensitivity. In examining a powdered preparation in which the orientation of the surfaces is heterogeneous, an observer sensibly chooses those parts of fragments which

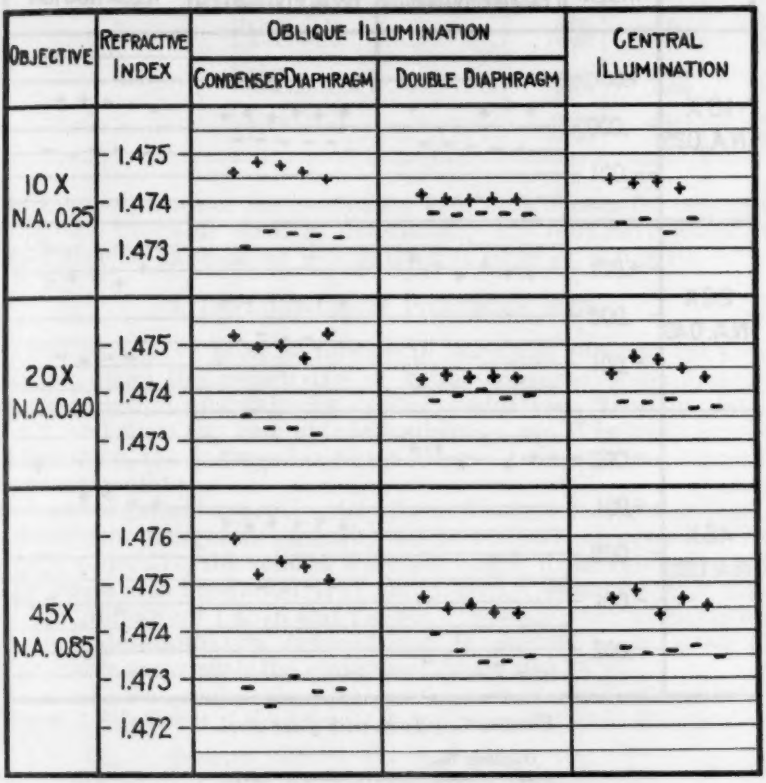

FIGURE 5.—*Tests with crushed borosilicate laboratory glass.*

Particles roughly equidimensional, diameter approximately 85μ.

show the most distinct phenomena. For such a reason, the results reported in this paper for crushed glass by the method of central illumination showed about the same sensitivity as did the results for potassium chloride. The explanation of Becke is the true one, and statements like that in a book review by Tunell and Morey[10] are founded upon an error concerning the origin of phenomena really observed in practical petrographic identifications.

[10] J. Am. Chem. Soc. **54**, 2575 (1932). They write, "The phenomena observed under the microscope with central illumination of powdered grains immersed in a liquid, sometimes called the 'Becke' line, are improperly so-called; the expression, 'Becke line' was coined by Salomon to designate the phenomena associated with total reflection at a vertical interface, which differ in theoretical interpretation from the phenomena obtained with central illumination of irregular grains; the latter are properly known as the central illumination effect."

(e) Neither method of oblique illumination exhibits so much dependence upon particle shape as the Becke line method.

The data presented in figures 3, 4, 5, and 6 represent conditions of failure to match. Visible optical phenomena indicate that the index of the immersion fluid lies either above or below that of the

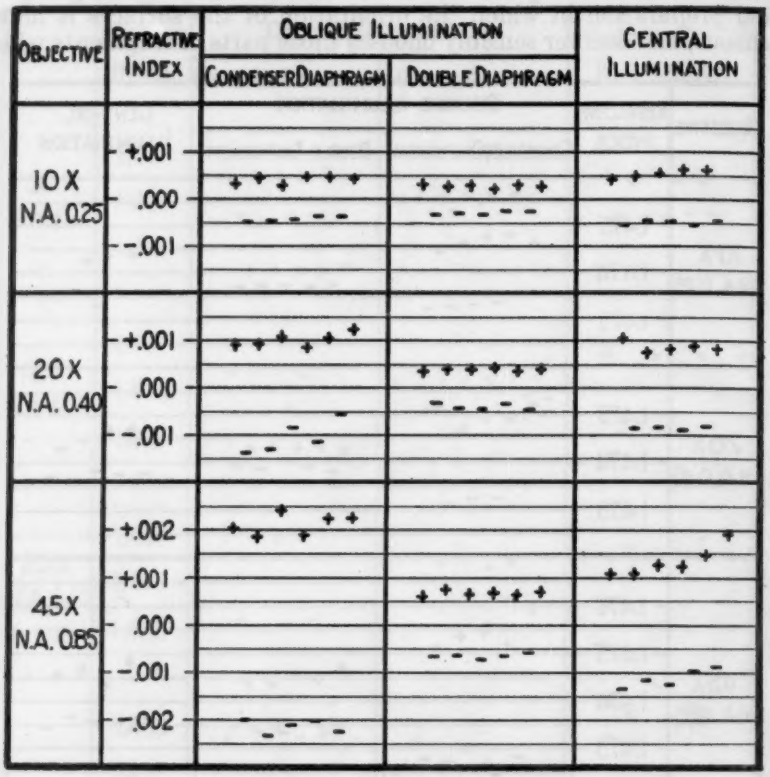

FIGURE 6.—*Tests with glass wool.*

Diameter 30μ.
Approximate refractive index, $n=1.517$.

material studied. In a practical determination of refractive index by the common procedure of changing liquids until one is found in which the immersed particle is invisible, the probable error at match would be approximately one-fourth [11] of the difference between the upper and lower rows of points. On this basis table 1 has been formed. It lists the probable errors of single determinations by matching of substances shaped like alum and potassium chloride.

[11] The usual probability relations do not apply in this case. When a particle is being matched, the properties of the liquid are not ordinarily varied continuously. Instead, the particle is compared with previously prepared mixtures. After invisibility has been secured there is no greater likelihood that the true index lies in one part than another of the zone of uncertainty.

TABLE 1.—*Probable error of a single determination resulting from uncertainty of match*

Objective	Substance	Oblique illumination		Central illumination
		Single diaphragm	Double diaphragm	
3.2×	Alum	0.00023	0.00008	0.00020
	KCl	.00026	.00014	.00023
10×	Alum	.00021	.00011	.00041
	KCl	.00027	.00016	.00022
20×	Alum	.00049	.00019	.00042
	KCl	.00048	.00020	.00017
45×	Alum	.00088	.00062	.00104
	KCl	.00125	.00037	.00045

As a consequence of the conditions which are chosen for estimating match, the probable error in determining the refractive index of a crystal may be as small as ± 0.0001 or as large as ± 0.0010.

8. INFLUENCE OF PARTICLE SIZE

A few tests have been performed to learn the effect of the size of particles upon the sensitivity of refractive-index determinations. Since the results qualitatively verified deductions from the data of table 1, and since any complete investigation would be most involved and fatiguing, the findings have been allowed to remain in a somewhat fragmentary state.

Spheres of glass,[12] approximately 2 μ in diameter, were examined by the double-diaphragm method with the 10 and 45× objectives. With the 10× objective, the spheres were not visible if the refractive index of the liquid was between 1.4711 and 1.4733. With the 45× objective, the limits were 1.4676 and 1.4745. In table 2 the probable error of a single determination deduced from these data is compared with the probable error with the glass wool (diameter 30 μ).

TABLE 2.—*Influence of size upon the probable error of a single determination*

Objective	Glass wool 30 μ diameter	Glass spheres 2 μ
10×	0.00014	0.0006
45×	.00034	.0017

By using particles one-fifteenth the diameter, the probable error has increased approximately fivefold. Obviously this rate of change must increase more rapidly as the limit of resolution is more nearly approached and thus the probable error become so large as to lose all meaning when the particles are irresolvable.

[12] These spheres of borosilicate laboratory glass were made by Dana L. Bishop, who has described their preparation. BS J. Research **12**, 177 (1934) RP642.

Determinations of refractive index by immersion are always made under bad conditions of resolution—the iris diaphragm is nearly closed, a stop in the condenser allows only the most oblique light to enter, or a diaphragm in the objective excludes most of the light which has not already been stopped by a diaphragm in the condenser. Down to a point where it becomes difficult to make out forms, the size of a particle does not have much influence, but for particles smaller than this the sensitivity falls off rapidly. Then, it is only by relaxing some of the conditions imperative for high sensitivity that resolution itself can be secured. Thus it is that those methods which are most effective with large particles permit the greatest sensitivity with particles near the limit of resolution.

II. ERRORS ORIGINATING IN THE BIREFRINGENCE OF CRYSTALS

In determining refractive indices by immersion methods, petrographers usually assume that the light vibrates normally to the axis of the microscope. They assume, in other words, that under all circumstances the beam of light is so little oblique that negligible errors are introduced by disregarding its inclination. Obviously there are no errors when, as in section I the substances investigated are isotropic. Just as obviously, the errors will be negligibly small when the birefringence is sufficiently slight. But substances of strong birefringence make up a large proportion of the cases in which the values of fundamental optical constants have been disputed.

Under a number of conditions it is possible to calculate [13] sufficiently well the errors which will result from assuming the light to be axial when, in reality, it is a composite of rays traveling many paths of greater or less inclination. The actual determination is a subjective integration of the information supplied by all these rays. When the difference between their errors is small as compared with the average error, it is satisfactory to simplify the mathematics and compute an average value. Otherwise the information may be gleaned more satisfactorily by a series of experiments. To accomplish this the errors generated by birefringence were studied on an actual crystal as functions of the numerical aperture of the objective, the criterion of match, and the relation between the plane of obliquity and the direction in the crystal corresponding to the refractive index being determined.

Mercuric cyanide crystallizes in the tetragonal system. When grown on the microscope slide it almost invariably rests upon a prism face. End forms are reasonably numerous, there being first- and second-order pyramids and possibly also sphenoids and pinacoids, but their descriptions are not pertinent to this investigation. Mercuric cyanide is strongly birefringent and uniaxial negative. The value of ϵ falls in a region served by one of the most satisfactory of immersion liquids, dibutyl phthalate. Since the birefringence of the compound is so extreme, $\omega-\epsilon=0.1563$, and since the limiting value ϵ can be determined only by using rays which travel in the basal plane of the crystal (which is perpendicular to the stage of the microscope),

[13] In a theoretical discussion, F. E. Wright, J. Wash. Acad. Sci. 5, 105 (1915), calculated the errors which should be caused by birefringence when the method of central illumination and the ordinary method of oblique illumination are employed. In the main, the effects which he calculated are consistent with those found experimentally in this study, but divergences with high-power objectives are of such magnitude that they ought not be neglected.

any deviation from this plane has a relatively large effect upon the apparent value of ϵ. Mercuric cyanide proved, therefore, to be almost ideally suited for these tests. With other substances, it is to

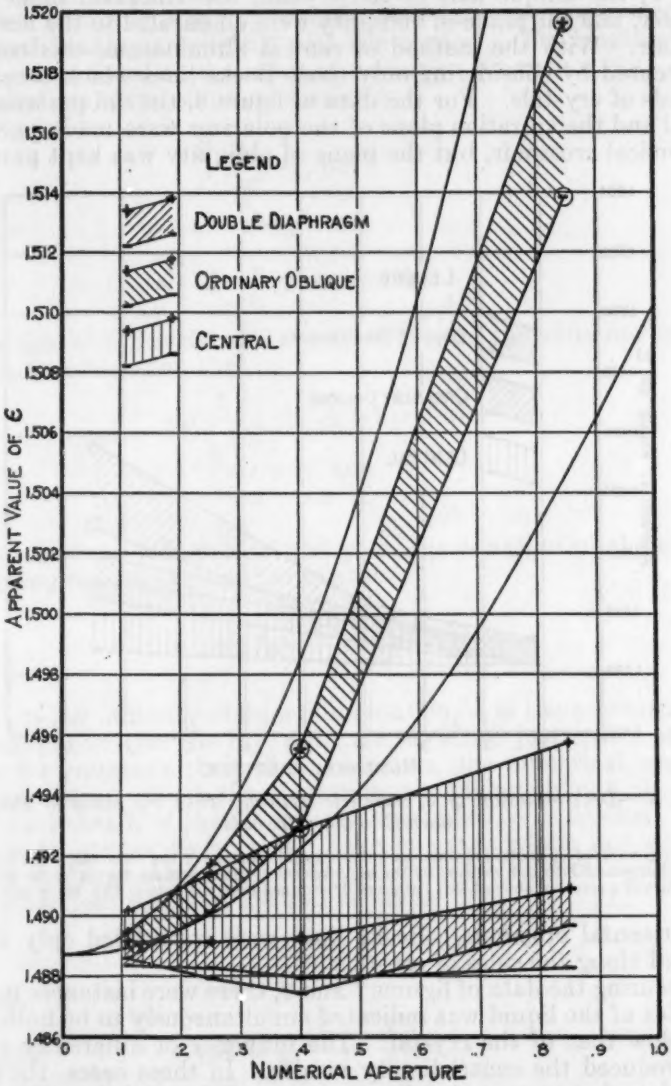

FIGURE 7.—*Determination of ϵ, mercuric cyanide, when the plane of obliquity contains the optic axis.*

The apparent value of ϵ is plotted against the full numerical aperture of the objective. The inaccuracies that are introduced into each method by the birefringence of the crystal are shown by the amount that the average of a zone lies above 1.4887 (true ϵ as determined from the data of this figure and figure 8). Calculated values for the ordinary method of oblique illumination are plotted as smooth curves.

be expected that errors will differ approximately in proportion to the birefringences.

Following the general procedure of section I, ϵ of mercuric cyanide was bracketed by the three methods of matching, and the same four objec-

tives, as well as for two orientations of the plane of obliquity with respect to the vibration direction being investigated. The data are presented in figures 7 and 8. To secure the results represented in figure 7, the unique axis of the crystal, the vibration plane of the polarizer, and the plane of obliquity were all parallel to the horizontal crosshair. With the method of central illumination, this condition was secured by considering only those Becke lines which occurred at the ends of crystals. For the data of figure 8, the unique axis of the crystal and the vibration plane of the polarizer were made parallel to the vertical crosshair, but the plane of obliquity was kept parallel to

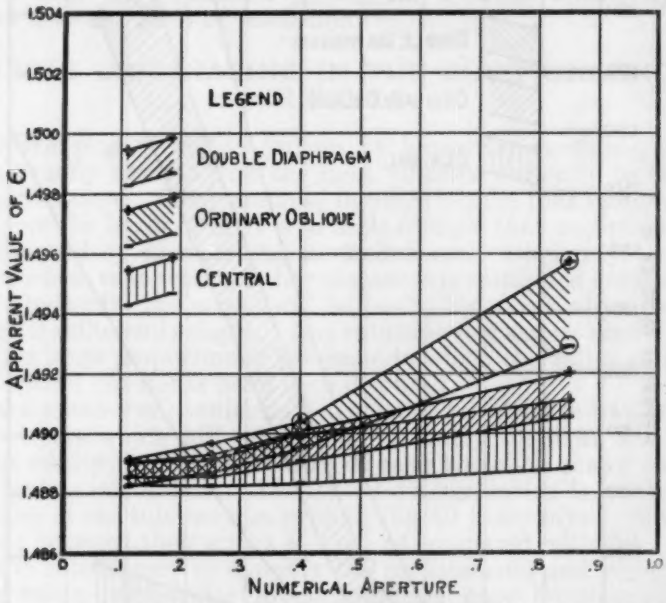

FIGURE 8.—*Determination of ε, mercuric cyanide, when the plane of obliquity is normal to the optic axis.*

The apparent value of ε is plotted against the full numerical aperture of the objective. The inaccuracies that are introduced into each method by the birefringence of the crystal are shown by the amount that the average of a zone lies above 1.4887 (true ε as determined from the data of this figure and figure 7).

the horizontal crosshair. Becke lines were considered only as they occurred along the sides of crystals.

In securing the data of figures 7 and 8, there were instances in which the index of the liquid was indicated simultaneously to be both above and below that of the crystal. The influence of differently oblique rays produced the contradictory results. In these cases, the refractive index of the immersion liquid was carried to a value that caused one of these effects clearly to predominate, though the other effect might still be marked. Such points in the figures have been indicated by circles drawn around them.

Besides the experimental points, two theoretical curves have been drawn in figure 7 to represent apparent values of ε by ordinary oblique illumination. In the vertical elliptical principal section, figure 9, through the index ellipsoid of mercuric cyanide, the horizontal half-

axis is proportional to ϵ, since the unique axis of the crystal lies in the plane of the microscope stage, and the axis perpendicular to ϵ is proportional to ω. The axes ϵ and ω correspond to directions of vibration and not of propagation. The ray travelling in the plane of this section and vibrating along ϵ_1, would travel in an isotropic medium along a path making an angle A with the vertical. The length of the line ϵ_1, is proportional to the index of refraction for such a ray.

The equation of the elliptical section is

$$\frac{x^2}{\epsilon^2}+\frac{y^2}{\omega^2}=1, \text{ but}$$

$$\epsilon_1{}^2=x^2+y^2 \text{ and}$$

$$\sin A=\frac{y}{\epsilon_1},\ y=\epsilon_1 \sin A.$$

By refraction at the surface of a preparation, α, the obliquity of the ray in air becomes such that

$$\sin \alpha=\epsilon_1 \sin A, \text{ wherefore}$$
$$y=\sin \alpha$$
$$y^2=\sin{}^2\alpha, \text{ and}$$
$$x^2=\epsilon_1{}^2-\sin{}^2\alpha.$$

Substituting these values of x^2 and y^2 in the equation of the ellipse and rearranging, we acquire the relation

$$\sin{}^2\alpha=\frac{\epsilon_1{}^2\omega^2-\epsilon^2\omega^2}{\omega^2-\epsilon^2}$$

in which, using ordinary oblique illumination, ϵ_1 is the extraordinary index of refraction for the ray, a, figure 10, which just enters or fails to enter the equatorial belt of an objective, the numerical aperture of which is sin α. When the diaphragm producing oblique illumination is so set that $\frac{4}{5}$ of the diameter of the objective is blocked, $\frac{1}{10}$ of the radius is open or $\frac{6}{10}$ is closed. For the rays which just succeed or fail in entering the objective at the points b and b^1, sin $\alpha=0.6$ N.A. Wherefore we have the two relations

$$N.A.=\sqrt{\frac{\epsilon_1{}^2\omega^2-\epsilon^2\omega^2}{\omega^2-\epsilon^2}}, \text{ and}$$

$$N.A.=\sqrt{\frac{\epsilon_1{}^2\omega^2-\epsilon^2\omega^2}{\omega^2-\epsilon^2}}\times\frac{1}{.6},$$

which were used to plot the smooth curves in figure 7.

The zone between the two curves corresponds to results which would simultaneously be indicated by different parts of the objective aperture if the method of matching were absolutely sensitive.

From the figures 7 and 8 it is readily apparent that errors can become excessively large. Ordinary oblique illumination and central illumination produce larger errors when the plane of obliquity is parallel to the vibration direction. The double-diaphragm method produces larger errors when the plane of obliquity is normal to the vibration direction. Errors can be kept small by an intelligent use of either the Becke-line method or the double-diaphragm method. Errors become greatest when the plane of the polarizer is parallel to the horizontal crosshair, a setting which has been recommended as producing the brightest images with daylight, and the ordinary method of oblique illumination is applied by swinging the mirror to one side or shading one side of the condenser with the finger.

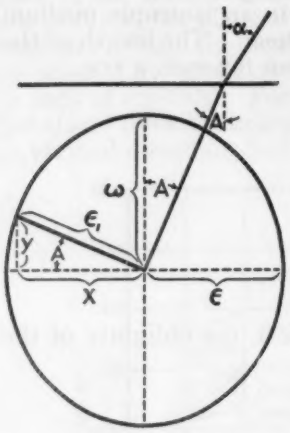

FIGURE 9.

A uniaxial crystal with its unique axis parallel to the microscope stage was used in the foregoing tests because the errors in determining an index could be easily analyzed and interpreted. If a uniaxial crystal otherwise oriented or a biaxial crystal had been chosen instead, interpretation would have been made more difficult by the more complex dependence of the apparent index upon the azimuth as well as the inclination of the many rays in the cone of illumination. But the inferences to be drawn from such tests would have been the same and the same recommendations of procedure would have resulted.

III. CONCLUSIONS

The ordinary method of oblique illumination should never be employed unless, as in preliminary trials, inexact results will suffice.

All the methods are capable of greater accuracy and higher sensitivity when employed with objectives of low numerical aperture.

The double-diaphragm method has in general certain small advantages of accuracy and sensitivity over the Becke-line method. With the former, the plane of vibration of the light vector should always be parallel to the horizontal crosshair. With the latter, it should always be parallel to the vertical crosshair when those Becke-line effects are considered which occur along the right and left sides of the particle.

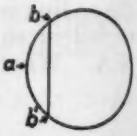

FIGURE 10.

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INFRARED ABSORPTION SPECTRA OF PLANT AND ANIMAL TISSUE AND OF VARIOUS OTHER SUBSTANCES

By R. Stair and W. W. Coblentz

ABSTRACT

Supplementing a previous report on plant pigments (BS Research Paper 617) the present paper describes new data on the infrared absorption spectra of plant and animal substances (cellulose and proteins) as found in nature and, in some cases, in the form of pure material prepared in the laboratory.

The data were obtained by means of a mirror spectrometer, portable vacuum thermopile, and ironclad Thomson galvanometer, described in previous publications. The region of the infrared spectrum extending to 15μ was examined.

Outstanding among the plant substances examined are samples of pure rubber, and associated materials—styrene, indene, polystyrene, and polyindene.

The cellulose materials examined included Cellophane (commercial preparation), onion skin, translucent membrane of pith of pokeweed, the seed septum of moonwort, and the seed wing of the cotton tree.

The protein materials examined included dried specimens of chitin (the outer integument of insects), pith of feathers, air bladder of fish, bat's wings, film of dried egg albumin, commercial gelatin, lining of egg shell, and wing of a dragon fly.

The miscellaneous substances reported upon are polyvinyl acetate and polyvinyl chloracetate resins, glyptal resin, shellac, and a group of substances of interest in connection with the Raman effect.

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I. INTRODUCTION

An important contribution to science is the determination of the effect of chemical constitution upon the spectral absorption of a substance.

Every substance, whether element or chemical compound, has a characteristic absorption spectrum. That is to say, the absorption spectrum of a compound is not the composite of the bands of selective absorption of the constituent elements. While this proposition is now accepted as axiomatic, it was an outstanding question among the early investigators in this field.

In recent years data on infrared absorption spectra have found important commercial and theoretical application, for example, the

Raman effect. Hence as time permits, and as characteristic material becomes available, data are being obtained on the infrared absorption spectra of various substances.

The present paper contributes new data to the gradually increasing store of information regarding characteristic absorption spectra of substances found in nature and, in some cases, prepared in a pure state in the laboratory. Among these substances are various forms of rubber, cellulose, and protein.

This paper gives data also on substances which were examined some years ago in connection with Raman's [1] [1] discovery that, in scattered radiation, the frequency difference between the companion line and the exciting line is constant and is equal to the frequency of an infrared absorption band.

The part of this investigation relating to plant pigments was reported in a preceding paper [2], to which reference is made for a condensed summary of the present-day theoretical aspects of infrared absorption.

It will therefore suffice to recall that the present-day conception of the mechanism of absorption assumes each absorption band to be a fundamental, a harmonic, or a combination effect, involving vibrational and rotational states of the molecule.

The earlier observations [11] of approximately harmonic absorption bands (for example the absorption bands of hydrocarbons, at 0.86, 1.71, 3.43, 6.86, and 13.8 to 14μ) have thus found a place in present-day speculations; but not, however, without some distortion of numerical values.

For example, some writers have used the value 6.90μ, (the maximum of an absorption band of hydrocarbons) because, as a fundamental, it fits the formula better than the observed value 6.86μ in spite of the fact that the best calibration data available indicate that the observed value is the more probable.

With the limited data at hand at that time, the most definite inference that could be emphasized by the earlier investigators was that certain absorption bands are caused by particular groups of atoms (for example CH_2, CH_3, OH, and COOH groups) although the bonding of the atoms (for example C=O) was also mentioned [3]. Recent writers, supplied with more varied data, are inclined to assign the cause of absorption principally to the bonding or linkage of the atoms, e. g., the "C-H linkage" or the "N-H linkage." This, of course, as already mentioned, was evident, but not stressed, in the earlier conclusions [4] on the effect of the arrangement of the atoms in the molecule (e. g., compounds having NCS or SCN radicles) and in the chain compounds where the position of the maxima of absorption remained unchanged whether the compound contained 6 C-atoms and 14 H-atoms or 24 C-atoms and 50 H-atoms [11]. In some cases the terms "groups" and "bonds" were used synonymously, showing looseness in terminology instead of actual differences in ideas.

The foregoing conclusions are based upon studies of substances having a fairly simple atomic structure. As was to be expected, subsequent studies of the absorption system of highly complex molecular structures, such as obtain in the aniline dyes [5], indicated so great a complexity that no definite conclusions could be drawn regarding the identification of certain absorption bands with certain

[1] Numbers in brackets refer to the list of references at the end of this paper.

groups of atoms. A similar condition was found in the absorption spectra of plant pigments previously reported [2] and in some of the herein-described substances.

II. INSTRUMENTS AND METHODS

Reference is made to previous publications [2, 6, 7, 8, 9] for a more detailed description of the experimental procedure.

The spectroradiometer consisted of a spectrometer with mirrors 50 cm in focal length. In some of the work a fluorite prism was used for exploring the spectrum from 1 to 7μ, and a rock-salt prism for the region of 7 to 15μ.

A portable vacuum thermopile of bismuth-silver, connected with an ironclad Thomson galvanometer, was used for measuring the spectral radiation. The source of radiation was a Nernst glower, focused upon the entrance slit of the spectrometer by means of a large concave mirror of 1 m focal length. The ratio of the galvanometer deflection observed when the specimen was placed in front of the spectrometer slit to the deflection observed when the material was out of the optical path gives the percentage transmission depicted in the illustrations. No correction was made for scattering, which accounts for the low values of the transmissions of the inhomogeneous materials in the short wave lengths.

The containers for the liquids or vapors were made of cleavage plates of rock salt or polished plates of fluorite, placed at the entrance slit. Variations from the standard procedure are noted in the text.

A very thin (capillary) film of a liquid was obtained by splitting a crystal of rock salt (size 5 by 3 by 1 cm) into two parts, each 5 mm in thickness, reassembling it accurately, and placing a drop of the liquid in a conical or V-shaped depression, cut into one side, along the line of cleavage of the crystal. By capillary action the film of liquid spreads uniformly, without interruptions by air bubbles, between the two plates.

The samples of animal and vegetable tissue were mounted over openings (5 to 8 mm wide by 15 to 20 mm long) cut into pieces of cardboard (index card), which were supported on a movable mounting in front of the entrance slit of the spectrometer.

The thicknesses of the samples were varied in order to produce greater contrasts between the absorption bands and the intervening more transparent parts of the spectrum. In certain cases where the material was deposited on a plate of rock salt, the thickness of the layer examined could not be accurately determined.

The data of interest in connection with the question of the Raman scattering of radiation were obtained on very pure materials (figs. 19 to 27, inclusive), some of which were prepared by Prof. J. Timmermans of the University of Brussels, Belgium, and deposited at this Bureau.

III. SPECTRAL-TRANSMISSION DATA ON PLANT AND ANIMAL SUBSTANCES

Under this caption are given the infrared spectral transmission curves of animal and vegetable (protein and cellulose) tissue, and, in some cases, of similar material after having undergone purification

(modification) in the laboratory. In view of the difficulty in procuring homogeneous material, the scope of the inquiry is necessarily restricted. Fortunately, a few natural plant and animal substances are available which, in the dry state, are relatively homogeneous.

1. RUBBER AND ASSOCIATED SUBSTANCES

Rubber is a hydrocarbon complex of CH, CH_2, and CH_3 groups. Hence, the freshly prepared material should and does show the bands of selective absorption characteristic of these groups of atoms.

The material examined was very generously supplied by W. Harold Smith [12], of the Chemistry Division of this Bureau, who purified the rubber by crystallization. The samples of ether-soluble (alpha) rubber and of the ether-insoluble (beta) rubber were prepared by a method of purifying and fractionating of rubber from Hevea

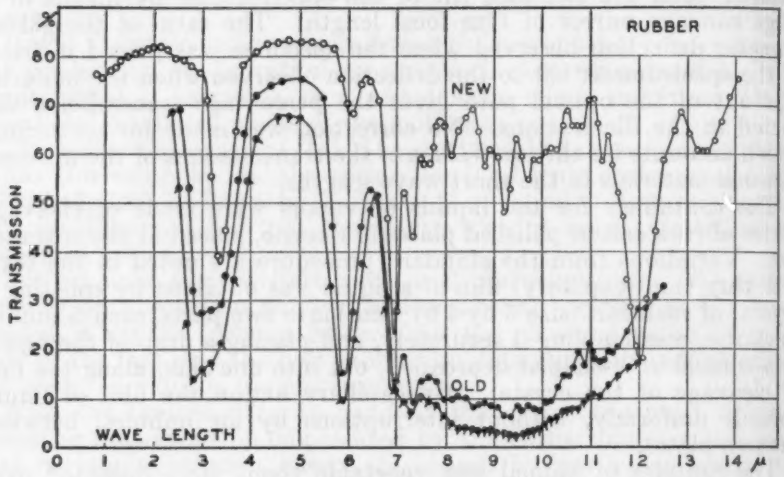

FIGURE 1.

latex, described in National Bureau of Standards Research Paper RP544 [12].

Suitable films were deposited from solutions of each fraction. Unfortunately, data on the undissolved, ether-insoluble fraction could not be included because films of this material, of the proper thickness, must be made by a special process, with apparatus that was not available.

The infrared transmission spectrum is of interest in connection with the study of the preparation of synthetic rubber or other material of similar physical nature.

(a) PURE RUBBER

In figure 1 are depicted the spectral-transmission curves of a film of rubber (containing the unseparated alpha- and beta-components, which were present in the ratio of 3:1, respectively) when freshly prepared and after aging for 7 and 16 months, respectively, in a glass container and at laboratory temperature.

The sample consisted of a solution of the rubber dissolved in a mixture of xylol and ether, a small amount of which was placed upon a plate of rock salt. The solvents were removed by keeping the rock-salt plate in an evacuated chamber for several days prior to the spectral examination.

In addition to the usual hydrocarbon bands at 3.43, 6.95 (usually 6.86), and at 7.3 μ, respectively, the small absorption band at 6 μ and the large band at 12.0 μ are to be noted.

As the sample changes by aging (oxidation) the infrared absorption is greatly changed. The strong absorption band at 12 μ is submerged by the heavy absorption throughout this spectral region.

On the other hand, the small absorption bands, in the region of 2.8 μ and at 6 μ (observable in the fresh material), which are indicative of hydrocarbons modified by OH-groups and oxygen, became the most

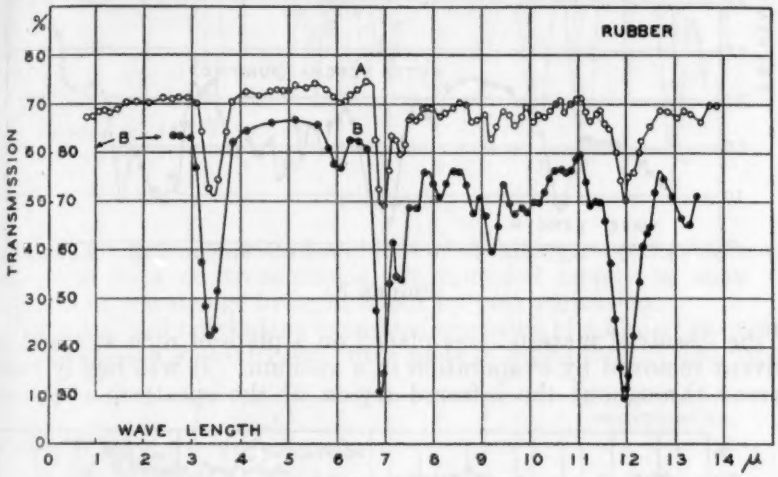

FIGURE 2.

conspicuous absorption maxima (at 2.9 and 5.9 μ, respectively) in the infrared spectrum of the aged material.

The spectral absorption of separated samples of alpha (A) and beta (B) rubber are illustrated in figure 2. The close agreement between these 2 curves and that of figure 1 is significant. Evidently, on the basis of this analysis, the two forms of rubber have a very similar molecular structure.

The large absorption band at 12 μ found in ethane, C_2H_6 [11] and the ever-recurring maxima at 3.45, 6.9, and 7.3 μ are to be noted.

An examination of a sample of the beta material, in the ultraviolet spectrum, indicated a high transmission extending from the visible region to 365 mμ. For wave lengths shorter than 365 mμ the sample showed a decrease in transmission to about 250 mμ, where it was completely opaque.

(b) PURE GUTTA-PERCHA HYDROCARBON

The sample examined was a translucent film about 0.07 mm in thickness. It was prepared by successive crystallizations from a solution in petroleum ether.

The spectral transmission curve is shown in figure 3. There is a close resemblance to rubber only for wave lengths shorter than 10 μ.

(c) PURE BALATA HYDROCARBON

This sample was purified by the same process employed with gutta-percha. A thin film (probably 0.01 to 0.02 mm thickness when dried)

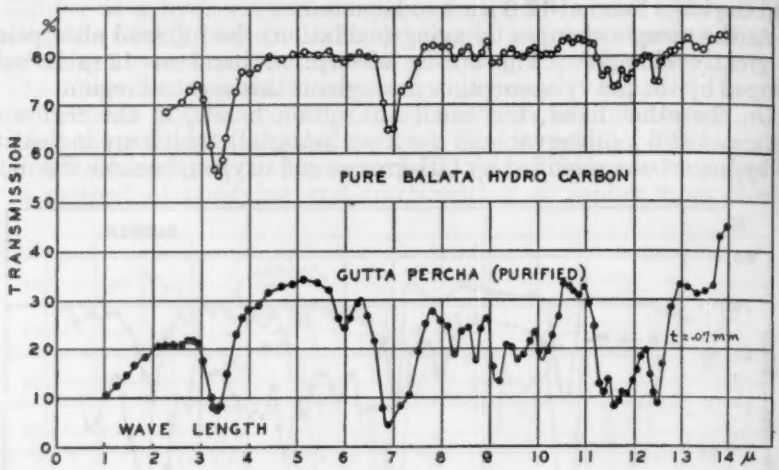

FIGURE 3.

of the dissolved material was placed on a plate of rock salt and the solvent removed by evaporation in a vacuum. It was highly transparent throughout the infrared region of the spectrum examined.

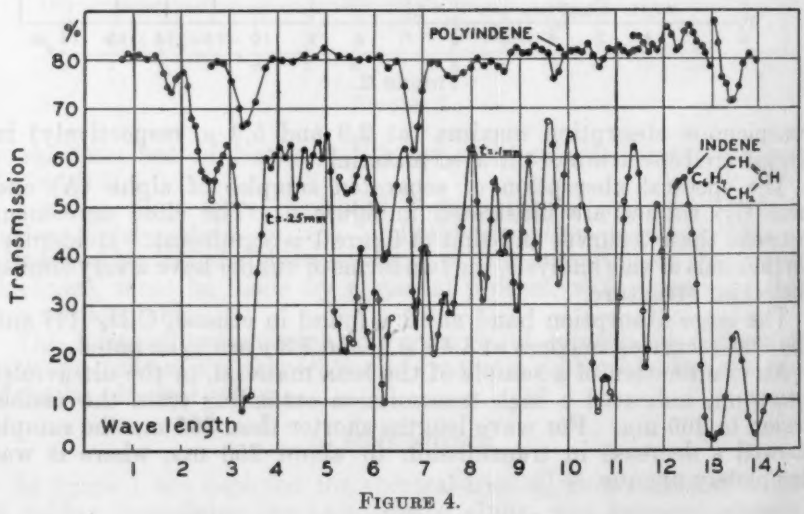

FIGURE 4.

The absorption bands (fig. 3) resemble very closely those of gutta-percha, which indicates a similarity in chemical constitution as found by chemical tests.

(d) POLYINDENE AND POLYSTYRENE

The polyindene (fig. 4) and polystyrene (fig. 6) were prepared by the action of 85 percent sulphuric acid at 0° C, using the method of Brooks and Humphrey [13]. The preparation of these polymers was

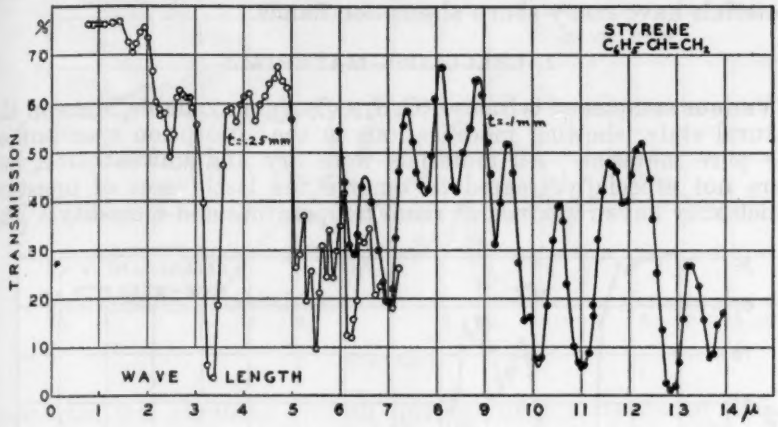

FIGURE 5.

not rigidly controlled with the object of obtaining reproducible material. The data on transmission are intended merely to show the direction of the change brought about by polymerization.

The sample of polyindene examined consisted of a film of the material (thickness about 0.01 mm) on a plate of rock salt. It was depos-

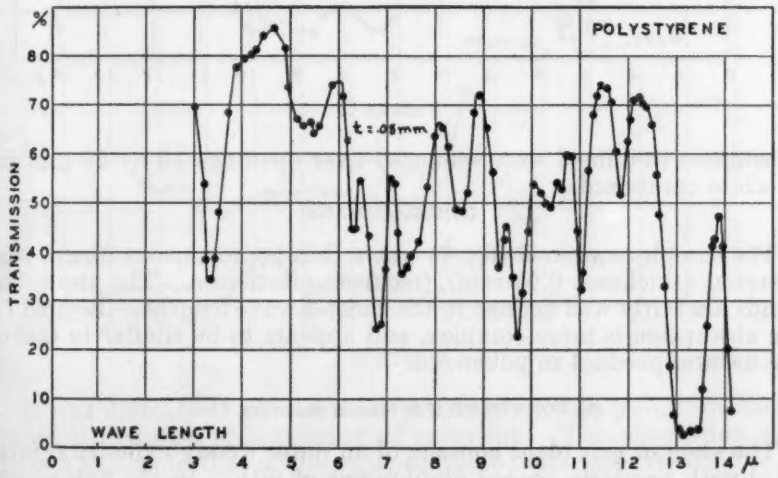

FIGURE 6.

ited with a volatile solvent which was removed by keeping the sample in a vacuum for several days.

A transparent film of polystyrene was prepared in a similar manner but removed from the plate. The sample (thickness 0.08 mm) was mounted over an opening in a cardboard for examination.

(c) STYRENE AND INDENE

The styrene (fig. 5) and indene (fig. 4) examined were pure materials having boiling points and densities in conformity with the values given by Beilstein [14]. Acknowledgment is due to the Ciba Co., Inc., New York, N. Y., for a sample of indene of high purity. Both materials have many sharp absorption bands.

2. CELLULOSE MATERIALS

Various samples of cellulose $(C_6H_{10}O_5)_x$ were available, some in the natural state, showing modifications in the absorption spectrum of the pure material. All materials were dry and unweathered, but were not especially treated to remove the last traces of moisture which may have remained at room temperature and humidity. The

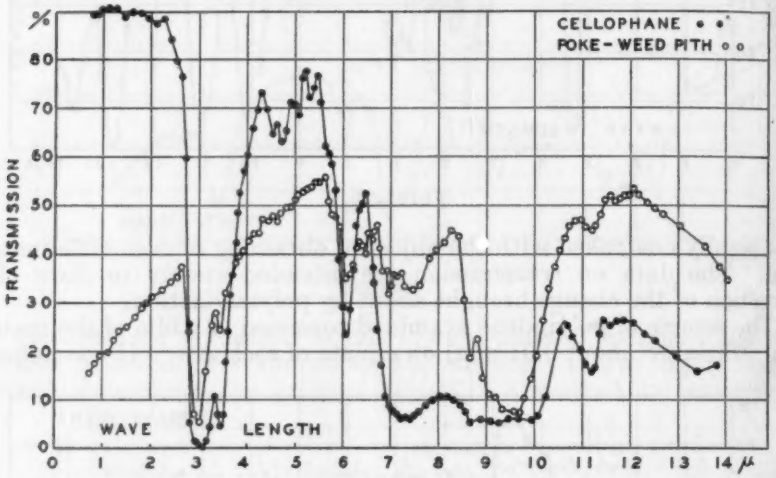

FIGURE 7.

substances examined were mounted over openings 10 by 20 mm cut in white cardboard.

(a) CELLOPHANE

The sample examined (fig. 7) was a thin homogeneous film of pure material (thickness 0.03 mm), free from plasticizer. The absorption bands are fairly well defined in the shorter wave lengths. Beyond 7 μ the absorption is more complex, and appears to be similar to that of the natural product in pokeweed.

(b) POKEWEED (*Phytolacca decandra*, Linn.)

The stem of this plant consists of an outer woody cylindrical tube, filled with regularly spaced diaphragms of pith. In the natural dry state the central portion of each diaphragm (1 to 2 cm in diameter) consists of a thin translucent membrane.

The absorption spectrum (fig. 7) closely resembles that of cellophane. The reduced height of the ordinates in the shorter wave lengths is the result of scattering of radiation by the pith, for which no correction has been made.

(c) ONION SKIN

Several specimens of onion skin were examined. Samples A and B (fig. 8) were pieces of dry integument from the outside of the bulb. Curve C depicts the spectral transmission of the thin membrane that grows between the fleshy scale-leaves of a young onion bulb. This

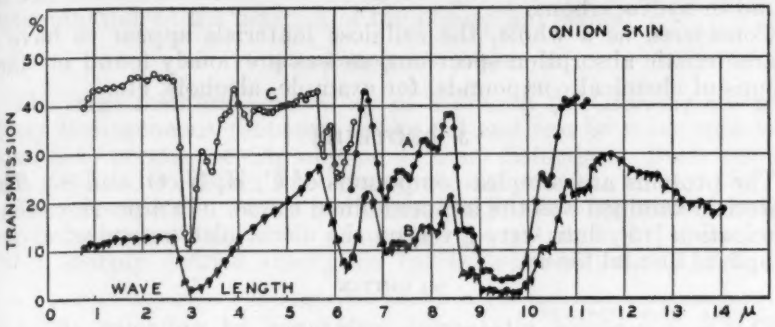

FIGURE 8.

membrane was mounted over an opening cut in a cardboard support and allowed to dry for 3 days before it was examined. The close resemblance between these transmission curves and those of Cellophane and of pokeweed pith is to be noted.

(d) SEED SEPTUM

The specimen examined was obtained from the seed pod of moonwort (*Lunaria biennis*), the longest dimension being about 25 mm.

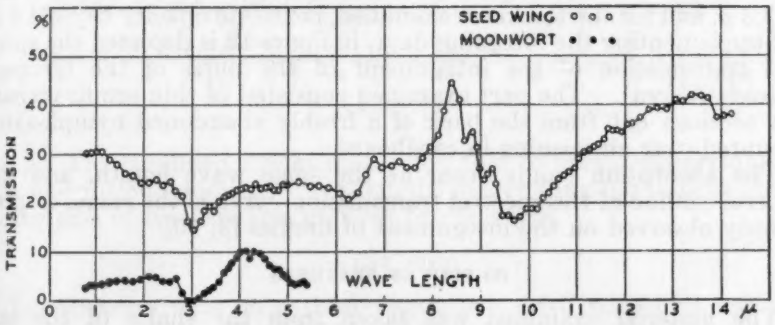

FIGURE 9.

It was difficult to obtain measurements on this (semitranslucent) material, because of scattering of radiation. The absorption spectrum is similar to that of the other cellulose materials examined.

(e) SEED WING

In figure 9 is depicted the spectral transmission curve of the delicate, silky, white, iridescent wing which is attached to the seed of the cotton tree (*Pithecoctenium echinatum*). The sample—which was collected by W. W. C. in Sumatra—was dry, and because of its large

size (4 by 8 cm) permitted an examination of a large area that was relatively homogeneous and transparent.

In this group of cellulose materials (one artificial, the others natural) the infrared absorption spectrum shows two strong bands, at 3 and 6.1 μ, respectively, which may be owing to the presence of moisture or perhaps OH-groups. Other bands (e. g., at 3.45 and 6.9 μ) are found in hydrocarbons.

Considered as a whole, the cellulose materials appear to have a characteristic absorption spectrum, as was previously found in other groups of chemical compounds, for example, alcohols, etc.

3. PROTEINS

The proteins are complex compounds of C, H, N, O, and S. The material examined was the impure animal tissue. In a previous communication [15], data were given on the ultraviolet transmission of a sample of animal tissue.

(a) CHITIN

This is a complex nitrogenous substance, of unknown chemical structure, which forms the outer, horny, amorphous integument of insects. In a previous communication [3, 10] infrared absorption spectra were given of the dried covering of the luminous organs of several species of fireflies. For completeness of exposition of the absorption spectra of proteins, reference to this earlier work is made in the present paper.

Aside from the inhomogeneity, and the brown color of some samples, which reduced the transmission in the visible spectrum, a conspicuous feature of the absorption spectrum of chitin is a relatively high transparency in the region of 1 to 2.5 μ, and, to a less degree, at 4 to 5.5 μ, with a strong complex absorption band (opacity) at 2.9 to 3.3 μ, and for the thickness examined, complete opacity beyond 6 μ.

Supplementing the foregoing data, in figure 12 is depicted the spectral transmission of the integument of the pupa of the lyreman (*Cicada tibicen*). The part examined consisted of thin semitransparent sections cut from the back of a freshly abandoned nymph-skin, mounted over an opening in cardboard.

The absorption bands occur at the same wave length, and the general outline of the spectral transmission curve is the same, as previously observed on the integument of fireflies [3, 10].

(b) PITH OF FEATHERS

The material examined was taken from the shafts of the tail feathers of a turkey buzzard, common about Washington. The individual sections of the pith, which are somewhat cylindrical in outline, and fairly translucent, were cut longitudinally and several such sections were spread out in a row over an opening (5 by 15 mm) cut in cardboard.

Transmission data on 2 samples of pith of feathers are given in figure 10. The transmission curves show two strong absorption bands, at 3 and at 6 μ, respectively. Beyond 6 μ the absorption consists of numerous fine lines. The low transmission at 1 μ is owing to scattering, for which no correction was made.

(c) FISH BLADDER

The air bladder of a fish (a croaker, taken from Chesapeake Bay), was examined after mounting over a perforated cardboard support and drying for several days.

The transmission curve (fig. 10) shows strong absorption at 3 and at 6 μ, but the material was too inhomogeneous to permit an accurate determination of the maxima of the absorption bands.

(d) DRAGON FLY WING

The large membraneous wings of a dragon fly (*Agrion*) are relatively homogeneous (between the veins) and can be made into windows that permit viewing objects without distortion. Such a specimen was used to obtain the data shown in figure 11.

The transmission curve is interesting in showing an absorption band at about 1.3 μ, which is unusual for a thin layer of material. Other sharply defined absorption bands occur at 3.0, 3.5, 6.1, and

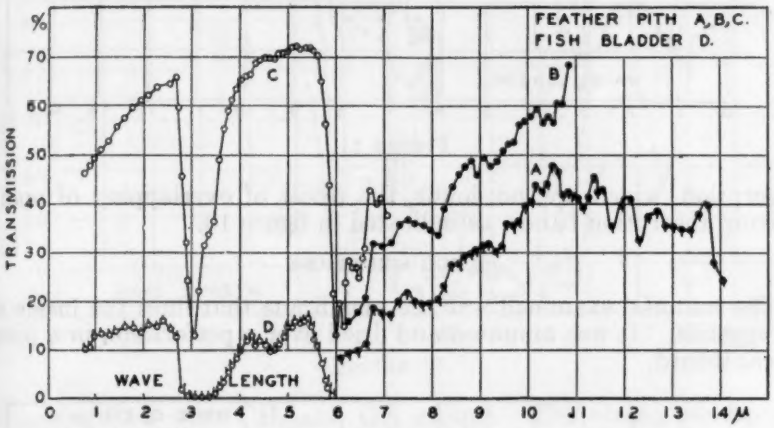

FIGURE 10.

6.5 μ. The specimen was evidently too thin to permit observing the fine absorption bands, at wave lengths longer than 6.5 μ, that occur in the pith of feathers and in other proteins [20].

(e) BAT WING

Transmission data on a thinly stretched, dried wing of a bat are given in figure 11. The highly diffusing character of the sample is evident by the general upward trend of the transmission curve between 0.8 and 5.5 μ. Strong absorption bands occur at 3.0, 3.5, 6.0, 6.1, 6.5, and 6.9 μ, in common with the other protein material examined.

(f) EGG ALBUMIN

In figure 12 is depicted the spectral transmission of a film of white of egg. The specimen was prepared by allowing a film of the egg albumin to dry upon a plate of quartz, from which it was peeled and mounted over a slit in a piece of cardboard.

The film was highly transparent in the visible and to 2.5 μ in the infrared.

There is a strong absorption band, with an unresolved maximum extending from 2.95 to 3.5 μ, and a similar band with maxima at 5.9, 6.0, and 6.2 μ. Beyond 7 μ the film shows wide bands of selective

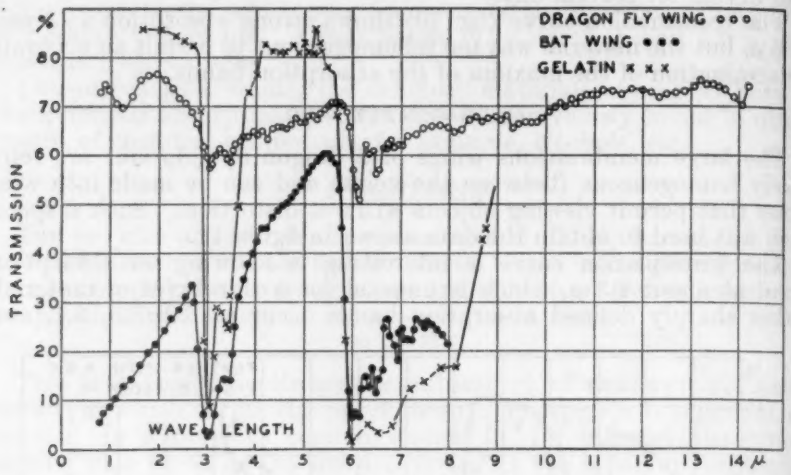

FIGURE 11.

absorption, which are, no doubt, the result of overlapping of many narrow absorption bands, as indicated in figure 10.

(g) EGG MEMBRANE

The material examined was the membrane that lines the inside of an eggshell. It was mounted and dried over a perforation in a piece of cardboard.

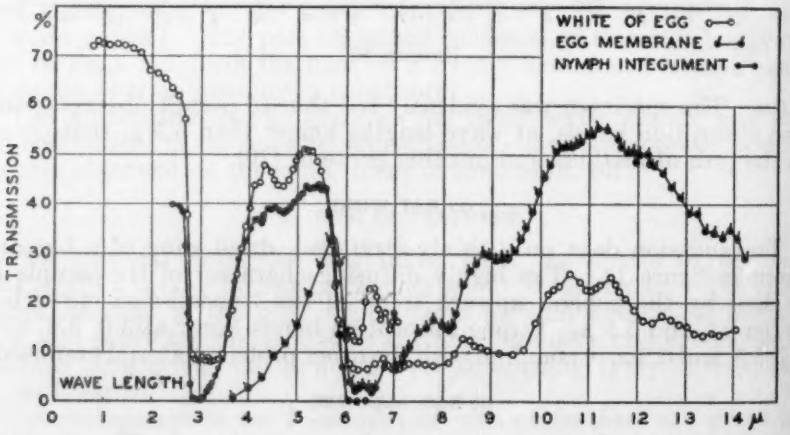

FIGURE 12.

Owing to the highly diffusing character of the material, no absorption bands could be identified for wave lengths shorter than about 6 μ (fig. 12). For longer wave lengths the absorption bands are similar to those of egg albumin and other proteins examined.

(h) GELATIN

This substance belongs to the albumins, the chemical composition of which is unknown. They contain C, H, O, N, and S. The transmission curve of dehydrated commercial material previously examined [3] is given in figure 11 for completeness of exposition of the subject.

Considered as a whole, the proteins examined exhibit a characteristic absorption spectrum (with individual differences of course) as previously observed in groups of chemical compounds, such as the carbonates, alcohols, and fatty acids.

Characteristic absorption maxima occur at 3.0, 3.43, 4.2 4.6, 5.9, 6.3, 6.8, 7.3, 8.1, 9.2, 11.0, and 12.2 μ. Some of these maxima have

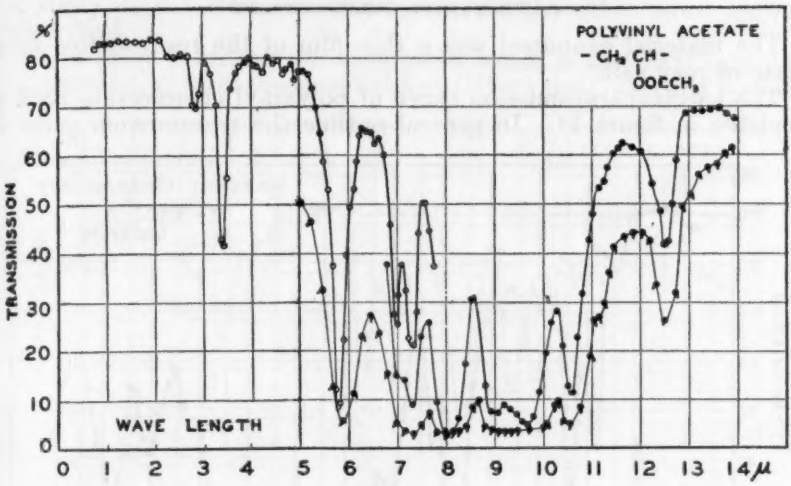

FIGURE 13.

been identified with CH_2 and OH groups. The strong absorption at 6 to 8 μ is noted in hydrocarbons modified by NO_2 groups.

IV. SPECTRAL-TRANSMISSION DATA ON MISCELLANEOUS SUBSTANCES

Under this caption are gathered the infrared spectral absorption curves of a number of compounds and substances which are of interest for miscellaneous reasons.

Some of the substances were examined in connection with a study of Raman's [1] theory of scattered radiation. Others have an interest in connection with the data on the rubber and cellulose materials. The examination includes also several newly developed synthetic resins, which have interesting absorption spectra. In several instances the substances were examined to obtain data in the spectral region of 12 to 15 μ not resolved in a previous examination [11].

1. VINYL RESINS

The basis of the vinyl (CH_2=CH) resins is ethylene, C_2H_4. They are amorphous, polymeric bodies formed by the action of ultraviolet light [16].

(a) POLYVINYL ACETATE

In figure 13 data are given on several samples of polyvinyl acetate resin. The specimens were prepared by melting some of the resin on, or between, plates of rock salt. In this manner a thin homogeneous film (probably 0.01 to 0.02 mm in thickness) of high transparency in the visible spectrum was easily obtained. This material has a high absorption between 7 and about 11 μ, as previously observed in ethylene [11]. However, the details of the absorption spectra are considerably different. For example, the prominent absorption bands at 3.28, 5.3, and 6.98 μ, respectively, in ethylene are shifted to 3.45, 5.8, 6.98, and 7.3 μ, respectively, in polyvinyl acetate.

(b) POLYVINYL CHLORACETATE

The material examined was a thin film of the resin melted on a plate of rock salt.

The spectral transmission curve of polyvinyl chloracetate resin is depicted in figure 14. In general outline the transmission curve is

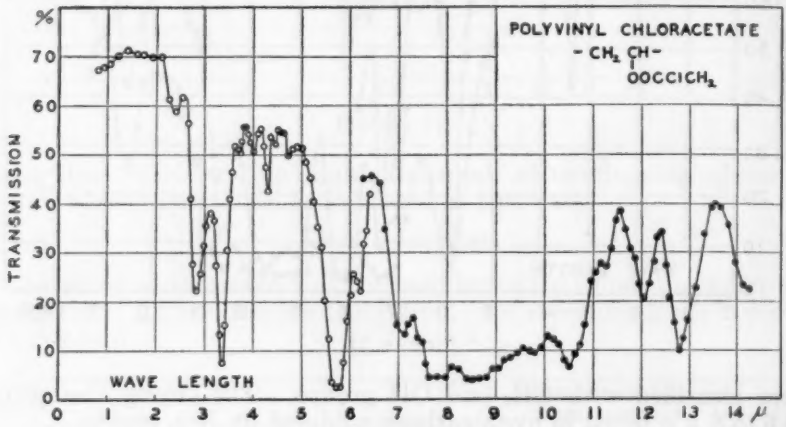

FIGURE 14.

similar to that of polyvinyl acetate, but at wave lengths longer than 7 μ the absorption maxima are different, particularly at 12 μ.

2. GLYPTAL RESIN

The name "Glyptal" is used [16] to designate resinous bodies that are produced from glycerol (a polyhydric alcohol) and organic acids—tartaric acid, citric acid, phthalic acid.

The point of interest in studying this substance is the effect of resinous condensation upon the hydroxyl groups, which, as previously observed [11], have a characteristic absorption at 2.9 to 3 μ.

The glyptal resin examined was obtained commercially as a white powder of unknown purity. Upon heating some of the powder (between rock-salt plates) in a bunsen flame a transparent film, tinged slightly yellow, was obtained.

The absorption spectrum, shown in figure 15, is quite different from that of the other two resins examined, as is to be expected.

The sharp absorption band at 2.9 μ, conspicuous in substances containing OH-groups, is to be noted. The less conspicuous bands at 3.43 and 6.86 μ, respectively, observed in substances containing CH_2 and CH_3 groups are also to be noted. The strong band at 5.8 μ has been found in numerous substances containing C=O linkages.

3. SHELLAC

Two samples of shellac (fig. 16) were prepared by melting some of the dry flakes of the commercial material on a plate of rock salt. The resulting film was very thin, showing only a trace of color. The spectral transmission of this material is of interest in connection with a study of the artificial resins and with the other plant materials examined.

Conspicuous among the absorption bands is the maximum at 2.9 μ observed in substances containing OH-groups; also the maximum

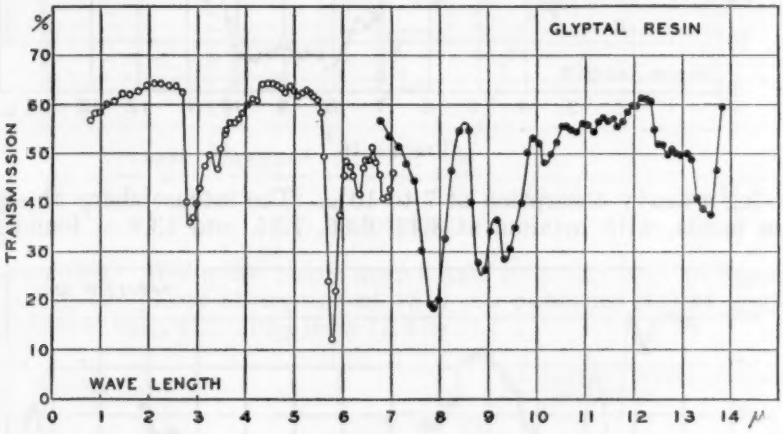

FIGURE 15.

at 5.85 μ in substances having C=O linkages; and the ever-recurring, approximately harmonic bands at 3.43, 6.86, (7.3) and at 13.9 μ observed in hydrocarbons containing CH_2 and CH_3 groups.

4. PARAFFIN OIL

The spectral transmission of a thick colorless paraffin oil (trade name Nujol) is given in figure 17.

The infrared transmission curve, with maxima of absorption at 1.8, 2.4, 3.43, 4.2, 5.8 to 6.2, 6.86, 7.3, 7.8, 8.7, 10.4, 11.2, 11.8, 12.4, 13.0, and 13.9 μ, is practically identical with that of the petroleum, distillates previously examined [11]. The spectral transmission, extending from 0.6 to 2.5 μ of a 1-cm layer of this oil is given in an earlier paper [17].

5. SPERM OIL

The sample of sperm oil (thickness 0.25 mm) was practically colorless. An examination of this substance was of interest in connection with earlier studies [3, 17] of other animal and of vegetable oils.

The infrared spectral transmission (fig. 18) differs mainly from that of the paraffin oils, and is similar to that of the fatty acids, in

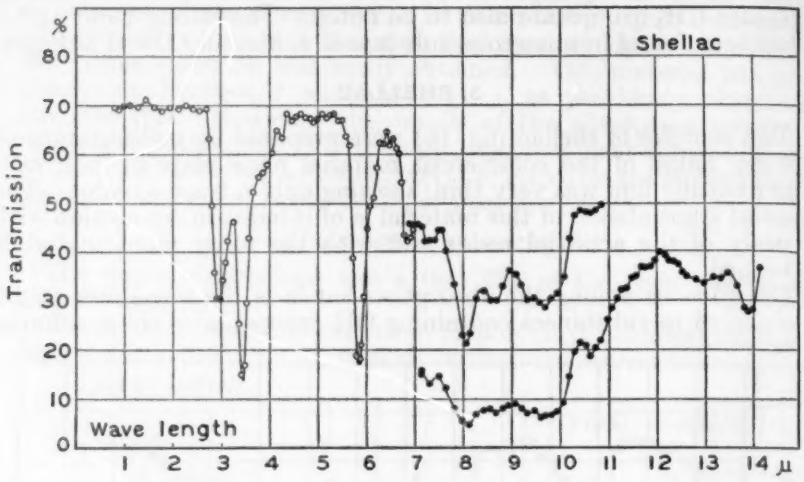

FIGURE 16.

having a heavy absorption at 7 to 10 μ. The intense sharp absorption bands, with maxima at 3.43, 6.86, 7.35, and 13.9 μ, found in

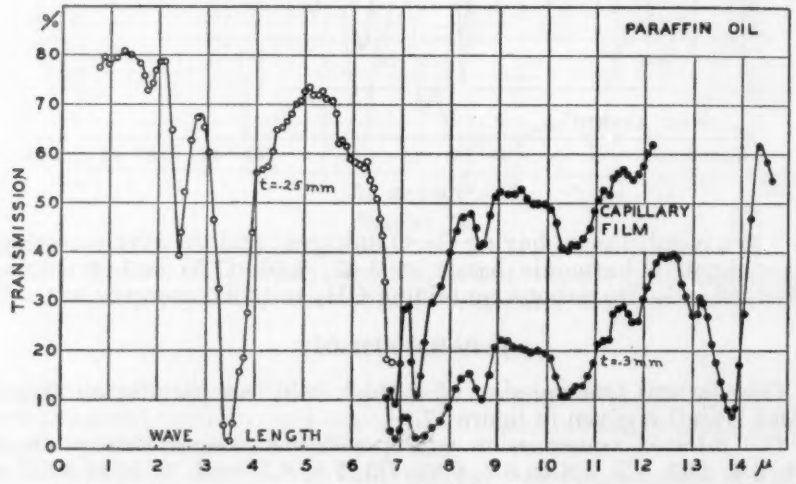

FIGURE 17.

hydrocarbons rich in CH_2 and CH_3 groups, and the band at 5.8 μ found in substances containing the C=O bond [3], are to be noted.

6. LINSEED OIL

This material was examined (fig. 19) to obtain a check on the spectrometer calibration and to extend the spectral range of earlier measurements [3] which stopped at 9 μ. The sharp maximum at 5.8

μ and the harmonic bands at 3.43, 6.86, and 13.9 μ were discussed in the earlier paper.

7. CARBON TETRACHLORIDE

Carbon tetrachloride was examined [19] in the spectral region between 7 and 14 μ (fig. 19) in connection with the study of Raman's

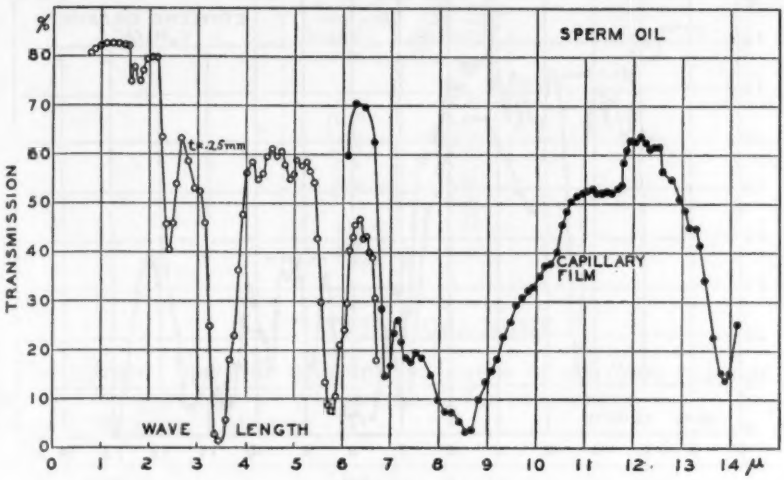

FIGURE 18.

theory [18]. While the bands near 8 and 10 μ had been previously mapped, the heavy absorption at 13 μ was published [11] as a wide unresolved band extending from 12.4 to 13.6 μ.

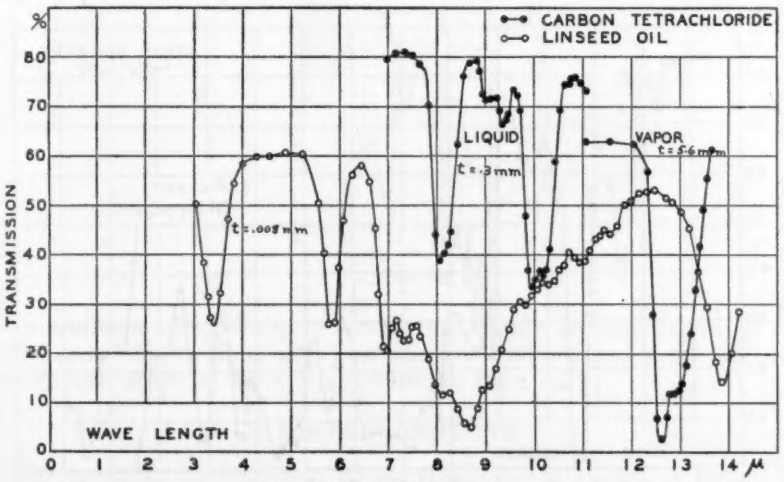

FIGURE 19.

In the region of 13 μ the absorption is so great that a conveniently produced thin, liquid film is completely opaque. An examination was, therefore, made of a column of the vapor (thickness 5.6 mm) which shows two absorption maxima in this region, at about 12.6 and 12.8 μ, respectively.

In this test the vapor was obtained by sealing a small amount of the liquid in a rock-salt cell, at room temperature and at atmospheric pressure.

The maxima of the strong absorption bands of carbon tetrachloride observed by Coblentz [11] and subsequently by Coblentz and Stair

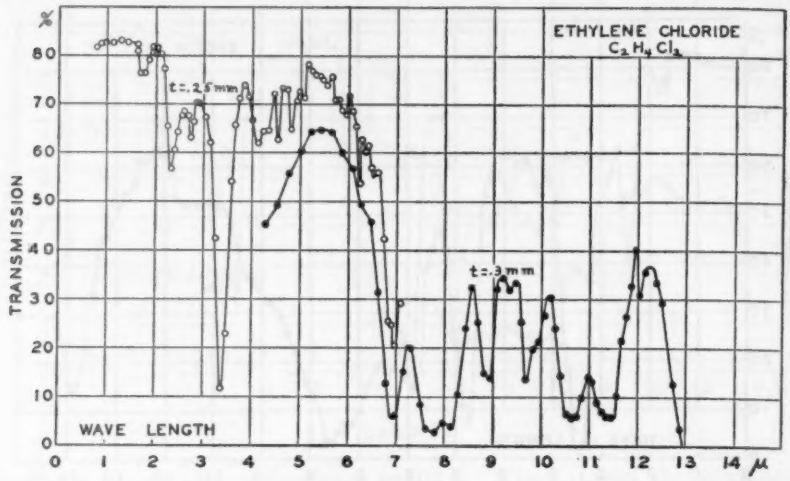

FIGURE 20.

[19] and the values calculated by Langer and Meggers [18] from their observations of the Raman scattering are given in table 1. The differences between the observed and the calculated values are entirely within the limits of accuracy of the observed data, which in some cases

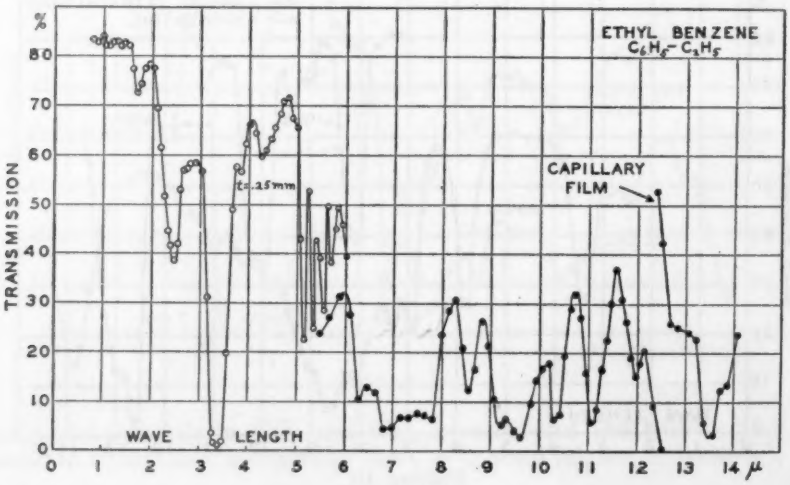

FIGURE 21.

suffer from lack of resolution of complex absorption bands. For example, if the band were completely resolved, the maximum absorption which appears to be at about 13.1 μ would, no doubt, be found at longer wave lengths. Again, the selective absorption at 9.0 to

9.5 μ may be a complex of three absorption bands, instead of two bands, as it appears from the transmission curve.

TABLE 1.—*Calculated and observed maxima of selective absorption of carbon tetrachloride*

Calculated (Langer and Meggers)	Observed (Coblentz and Stair)
μ	μ
13.18	13.10
12.66	12.67
10.23	10.22
9.92	9.95
9.20	9.32
9.06	9.08
8.21	8.20
8.01	8.02
6.59	6.57
6.50 6.46	6.45

8. ETHYLENE CHLORIDE

The infrared spectral transmission curve of ethylene chloride, is depicted in figure 20. It was examined for comparison with ethylene bromide previously studied [11].

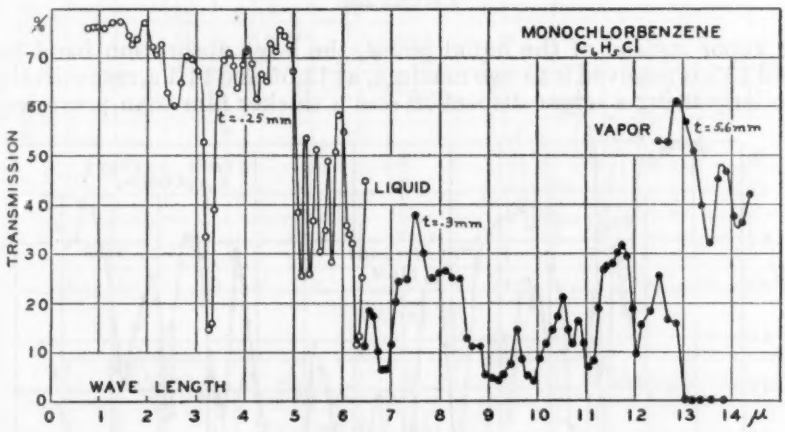

FIGURE 22.

In addition to the intense absorption bands in the region of 3.4 and 6.9 μ, observed in ethylene and its derivatives, there are new absorption bands at wave lengths longer than 8μ.

9. ETHYLBENZENE

The spectral transmission of ethylbenzene is shown in figure 21. This supplements the data previously published, particularly in the region of 5 to 6μ, where the use of a fluorite prism made it possible to resolve the selective absorption into a group of sharp bands not shown in the earlier work.

10. MONOCHLORBENZENE

The infrared transmission of monochlorbenzene depicted in figure 22, supplements the measurements previously published [11]. Using

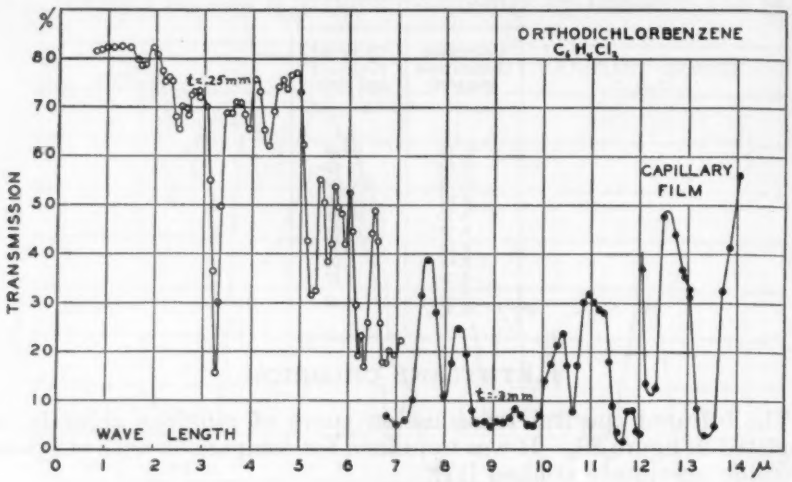

FIGURE 23.

the vapor instead of the liquid phase, the large absorption band beyond 13 μ is resolved into two maxima, at 13.55 and 14.1 μ, respectively. Similarly using a larger dispersion and a thicker film than previously

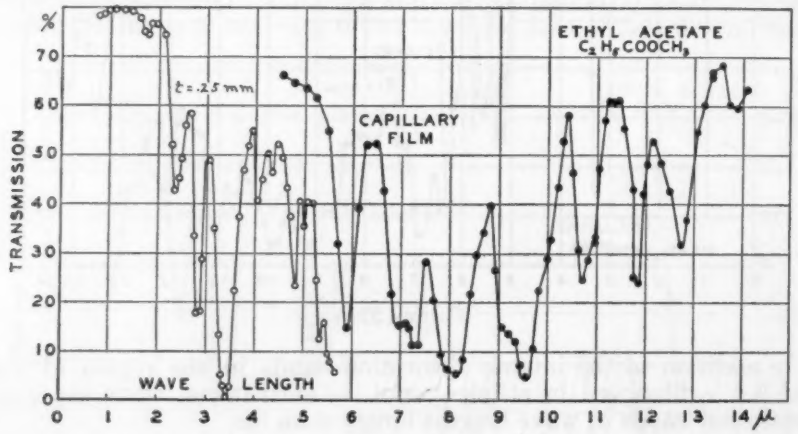

FIGURE 24.

employed, the selective absorption at 2 to 6 μ is resolved into numerous fine lines.

11. ORTHODICHLORBENZENE

In figure 23 is depicted the infrared spectral transmission of orthodichlorbenzene. The spectrum consists of numerous narrow bands of selective absorption, as in the preceding compound.

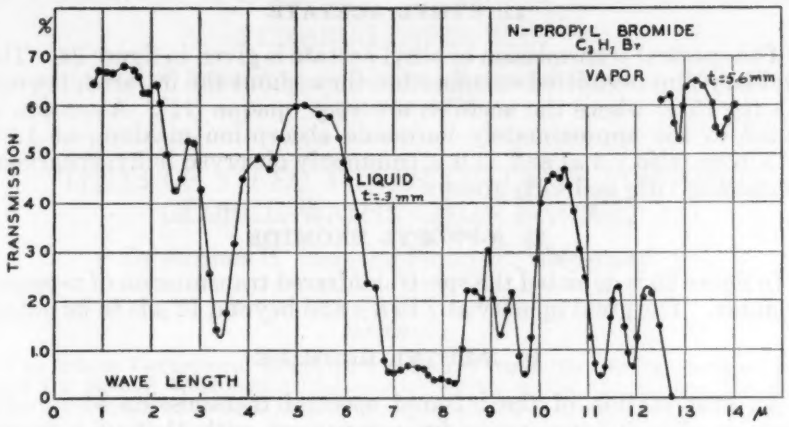

FIGURE 25.

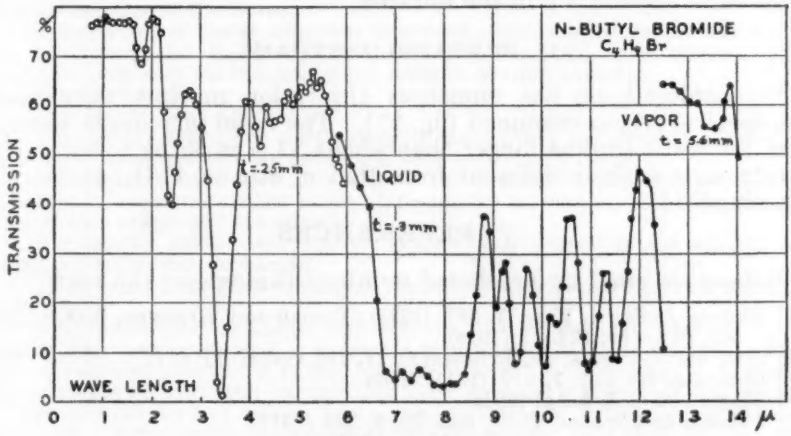

FIGURE 26.

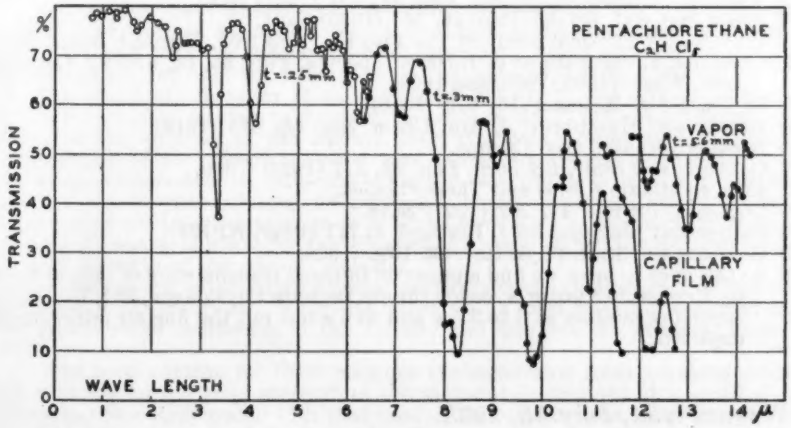

FIGURE 27.

12. ETHYL ACETATE

The spectral transmission of ethyl acetate is given in figure 24. The capillary film permitted examination throughout the infrared, beyond 5 μ (to 15 μ) where the acetates are very opaque [11]. Attention is called to the approximately harmonic absorption maxima, at 1.71, 3.43, 6.86 (also 7.3 μ) and 13.9 μ, commonly observed in hydrocarbons containing CH_2 and CH_3 groups.

13. *N*-PROPYL BROMIDE

In figure 25 is depicted the spectral infrared transmission of *n*-propyl bromide. The great opacity at 7 to 8 μ and beyond 12 μ is to be noted.

14. *N*-BUTYL BROMIDE

An examination of the infrared spectral transmission of *n*-butyl bromide (fig. 26) was made for comparison with that of *n*-propyl bromide, just described. Differences in the absorption spectra are observable beyond 8 μ in the infrared.

15. PENTACHLORETHANE

Pentachlorethane has numerous absorption maxima throughout the spectral region examined (fig. 27). The rapid increase in absorption for wave lengths longer than about 11 μ is to be noted. The spectrum is entirely different from that of ethane, C_2H_6, previously examined [11].

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WASHINGTON, July 15, 1935.

U. S. Department of Commerce National Bureau of Standards

RESEARCH PAPER RP831

Part of Journal of Research of the National Bureau of Standards, Volume 15, September 1935

TESTS OF STEEL TOWER COLUMNS FOR THE GEORGE WASHINGTON BRIDGE

By Ambrose H. Stang and Herbert L. Whittemore

ABSTRACT

The Bridge Department of the Port of New York Authority has designed and built the George Washington (suspension) Bridge across the Hudson River at New York City. The Port Authority requested the cooperation of the National Bureau of Standards in an investigation of the strength and other properties of the large fabricated steel columns. The columns were made of carbon steel, silicon steel, and carbon-manganese steel and were tested in the hydraulic compression machine at the Bureau.

The shortening of the columns was measured, using compressometers and electric telemeters, and the lateral deflection was measured at midheight. The tensile properties of the material were determined from coupons.

It was found that:

1. The loading was nearly axial.
2. For stresses within the elastic range of the column, the strains indicated by the compressometers and the telemeters were very nearly the same.
3. For stresses within the elastic range of the columns, there was no appreciable difference between the strains in the plates and in the angles, and therefore the stresses were practically the same.
4. For stresses which were nearly the maximum stresses in the column, the lateral deflection was very small.
5. There was no significant change in the relative positions of the main members under load.
6. The carbon-steel columns exhibited the phenomenon of pick-up, i. e., a definite first maximum load, a constant or slightly decreasing load for a considerable further shortening of the column, followed by a pick-up to a second higher maximum load after the columns were markedly deformed. The silicon-steel columns showed no definite first maximum load, but the load increased very slowly for a considerable shortening of the column and then more rapidly with further shortening. The carbon-manganese-steel columns showed no indication of more than one maximum load.
7. The column yield strength for the silicon-steel columns was 1.55 times that for the carbon-steel columns. For the carbon-manganese-steel columns it was 1.71 times that for the carbon-steel columns. These ratios are practically the same as the ratios of the average yield strengths of the materials.
8. The practical constancy of these ratios is shown by the column efficiency. For these columns having a slenderness ratio of 28.9, the column efficiency, defined as the quotient of the column yield strength divided by the weighted yield strength of the column material, was approximately 100 percent. For the carbon-manganese-steel columns the efficiency was 100 percent; for the carbon-steel and silicon-steel columns, 98 percent. These values are about the same as those observed in previous tests on columns having a slenderness ratio of about 40, when allowance is made for the effect of the speed of the testing machine on the yield strength of the column material.
9. At failure the outstanding angles buckled between diaphragms on the concave sides of the columns. No rivets failed. The local buckling occurred only after considerable shortening of the column and was not the primary cause of failure.
10. The tests confirm for these columns the conclusion from previous column tests that the tensile yield strength of the material determined at a speed of the testing machine comparable with that used in the column tests will furnish a close measure of the strength of short sturdy columns.

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I. INTRODUCTION

1. PURPOSE

The Bridge Department of the Port of New York Authority has designed and built the George Washington (suspension) Bridge [1] between Fort Washington, New York City, and Fort Lee, New Jersey. It crosses the Hudson River by a single span of 3,500 ft and two side spans of 610 and 650 ft.

Large box-section columns of silicon steel are an important structural element of the towers of this bridge. Because few tests have been made on large fabricated columns of silicon steel, information was desired on the strength and the behavior of these columns under load. The Port of New York Authority requested the National Bureau of Standards to cooperate in an investigation of the strength and other properties of these large fabricated steel columns.

[1] Eng. News-Rec. 21, 100, 819 (1928). Trans. Am. Soc. C. E., 97 (1933,) Pop 1818-1826)

The Bureau's hydraulic compressive testing machine having a capacity of 10,000 kips [2] is the largest testing machine in this country. The test columns therefore were designed to have a strength less than the capacity of this machine and a length not exceeding 24 ft, the longest specimen which can be placed in the machine using available equipment. Except for length, the test columns were models of the bridge members to a scale of about one-half the linear dimensions.

II. THE SPECIMENS AND THE METHOD OF TESTING

1. GENERAL

The specimens are listed in table 1 with their nominal dimensions and properties.

TABLE 1.—*Nominal dimensions and properties of the test columns*

Number of specimens tested	Symbol	Kind of steel	Cross-sectional area of steel	Length	Moment of inertia		Radius of gyration		Slenderness ratio	
					I_{x-x}	I_{y-y}	r_{x-x}	r_{y-y}	$x-x$	$y-y$
			in.[2]	ft	in.[4]	in.[4]	in.	in.		
2	TC1, TC2	Carbon	159	24	15,794	15,794	9.97	9.97	28.9	28.9
2	TS1, TS2	Silicon	159	24	15,794	15,794	9.97	9.97	28.9	28.9
2	TM1, TM2	Carbon-manganese	151	24	14,995	14,995	9.97	9.97	28.9	28.9

2. SYMBOLS

The following symbols were used for convenience in identifying the specimens:

Design T=Steel tower columns,[3] George Washington Bridge.

Material { C=Carbon steel. S=Silicon steel. M=Carbon-manganese steel.

The numbers 1 and 2 were used to designate the individual columns in each group. Thus, the column TS2 was one of the two duplicate steel columns fabricated from silicon steel.

The longitudinal pieces of each column, that is, the longitudinal plates and angles, were cut as shown in the cutting diagram in figure 1. Each longitudinal piece of the column was match-marked to correspond with the coupon cut from the same plate or angle, and the location of each piece relative to the position of the column in the testing machine was recorded.

3. TESTING MACHINE

All the specimens were tested as flat-ended columns in a vertical hydraulic compressive testing machine [4] having a capacity of 10,000 kips.

No precision apparatus was available for calibrating this machine to capacity. At various times, by the use of load and deformation reading on columns, comparisons had been made with the Emery machine (having a capacity of 2,300 kips) up to loads of 1,600 kips.

[2] One kip=1,000 lb.
[3] Approximatly scale models of the bridge members.
[4] Described in B.S. J. Research 3, 507 (1929) RP108.

Extrapolation to higher loads has been made by load-deformation curves on larger columns. It is believed that the error in the loads

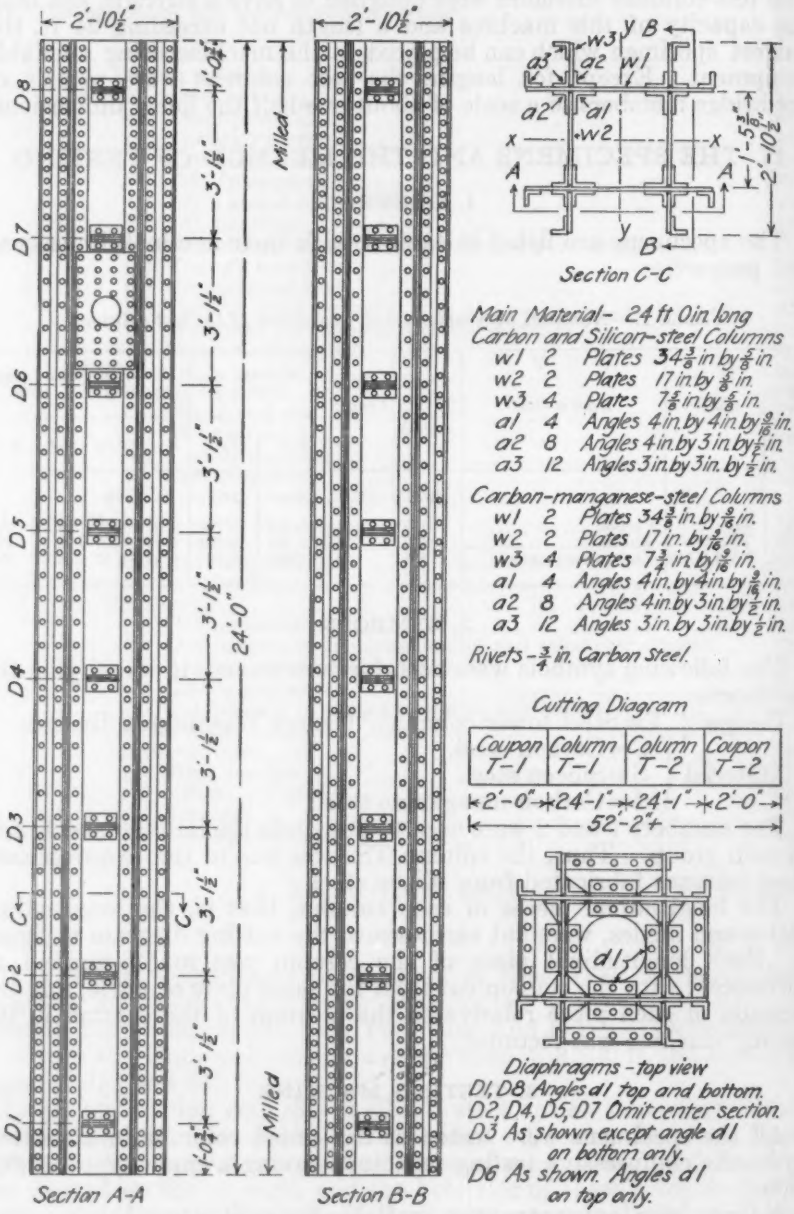
Section A-A
Section B-B
Section C-C
Main Material- 24 ft 0 in long
Carbon and Silicon-steel Columns
w1 2 Plates 34 3/8 in by 5/8 in.
w2 2 Plates 17 in by 1/8 in.
w3 4 Plates 7 5/8 in by 5/8 in.
a1 4 Angles 4 in by 4 in by 3/16 in.
a2 8 Angles 4 in by 3 in by 1/2 in.
a3 12 Angles 3 in by 3 in by 1/2 in.
Carbon-manganese-steel Columns
w1 2 Plates 34 3/8 in by 9/16 in.
w2 2 Plates 17 in by 9/16 in.
w3 4 Plates 7 3/4 in by 9/16 in.
a1 4 Angles 4 in by 4 in by 9/16 in.
a2 8 Angles 4 in by 3 in by 1/2 in.
a3 12 Angles 3 in by 3 in by 1/2 in.
Rivets - 3/4 in. Carbon Steel.
Cutting Diagram
Coupon T-1
Column T-1
Column T-2
Coupon T-2
2'-0"
24'-1"
24'-1"
2'-0"
52'-2"
Diaphragms - top view
D1, D8 Angles d1 top and bottom.
D2, D4, D5, D7 Omit center section.
D3 As shown except angle d1 on bottom only.
D6 As shown. Angles d1 on top only.

FIGURE 1.—*Dimensions of the test columns.*

on the columns for this investigation did not exceed 3 percent, and that the calibration of this machine did not alter by as much as 1 percent during these tests.

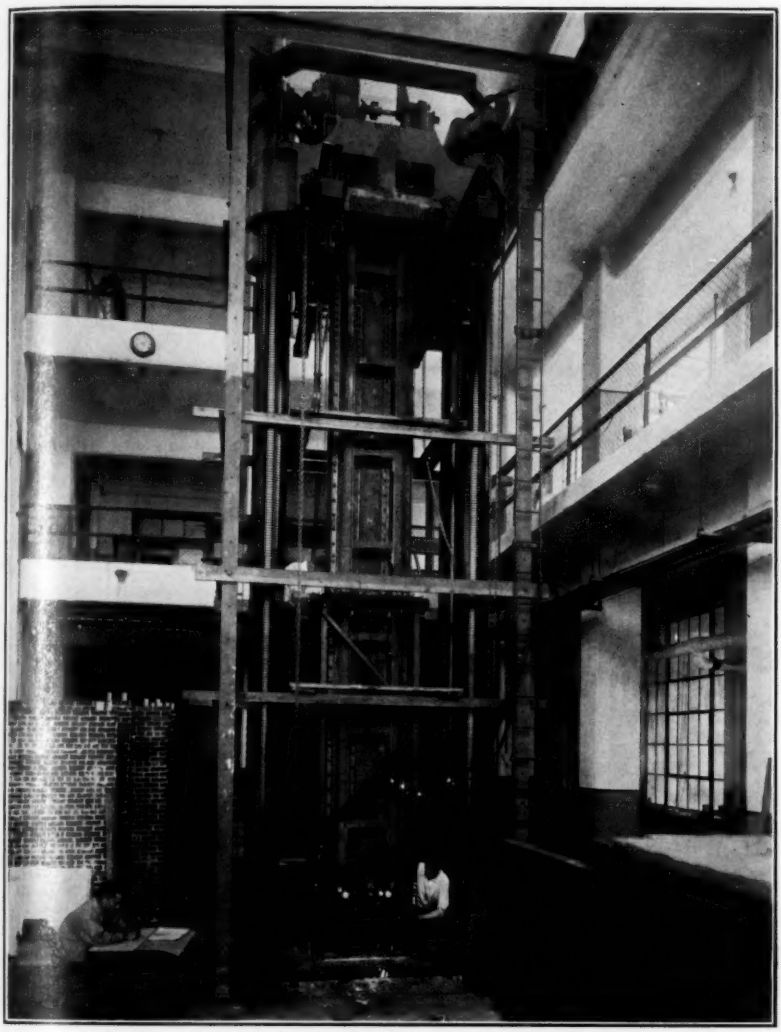

FIGURE 2.—*A column in the testing machine.*

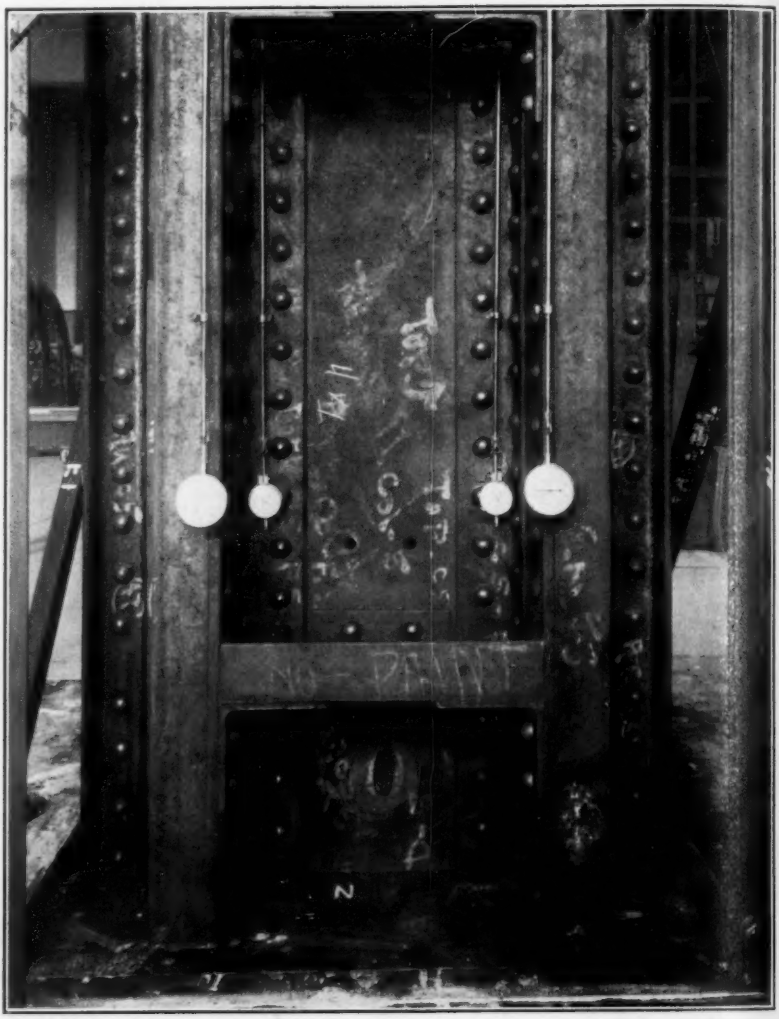

FIGURE 3.—*Lower end of compressometers on a column.*

The rods actuated the dial micrometers.

The loads were applied through steel bearing plates at each end of the specimen. A soft mixture of plaster of paris was used between the bearing plates and the platens of the machine to decrease local deformation of the plates.

The specimen was loaded to a stress not exceeding 10 kips/in.^{2} and the lower platen of the machine adjusted in its spherical seat until the load was axial as indicated by the readings of the compressometers.

4. THE TEST COLUMNS

(a) DESCRIPTION

The dimensions of the test columns are given in figure 1. It is apparent from section C-C that the cross section is symmetrical with respect to the centroidal axes x-x and y-y. The plates, w–1, were continuous across the column, but the corresponding plates parallel to y-y were in 3 pieces w–3, w–2, and w–3. There were holes in the plates w–1 to receive pins used for placing the column in the testing machine. The column was reinforced around the holes. Two of the columns were of carbon steel, two of silicon steel, and two of carbon-manganese steel.

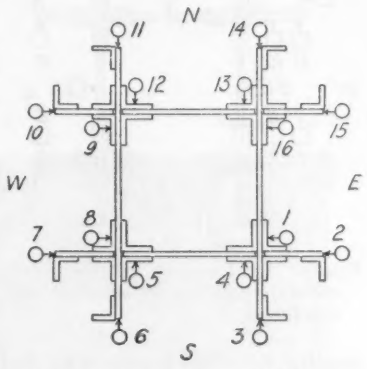

FIGURE 4.—*Location of the compressometers (indicated by circles) on a column.*

The nominal properties of these columns and of the columns in the George Washington Bridge towers are given in table 2. A steel test column in the testing machine is shown in figure 2.

TABLE 2.—*Nominal properties of the test columns and of the columns in George Washington Bridge*

Properties	Test column	Bridge column
Area, in.^{2}	159	716
Moment of inertia, in.^{4}	15,794	264,526
Length, ft	24	50
Radius of gyration, in.	9.97	19.2
Slenderness ratio (l/r)	28.9	31.2
Ratio $\frac{\text{Web thickness}}{\text{Web width}}$	$\frac{1}{15.0}$	$\frac{1}{7.9}$

(b) TESTING PROCEDURE

(1) *Compressometers.*—Compressometers having a gage length of 20 ft were used to measure the shortening of the columns under load. The middle of the gage length was at midheight of the column. The lower ends of the rods actuated dial micrometers attached to the column at the lower gage mark as shown in figure 3. One division on the dials was 0.001 in., and readings were estimated to 1/10 of a division. The location of the compressometers is shown in figure 4.

(2) *Telemeters.*—Eighteen telemeters [5] having a gage length of 8 in. were located on vertical gage lines near midheight of the columns,

[5] Proc. Am. Soc. Testing Materials [II] **23,** 592 (1923); Tech. Pap. BS **17,** 737 (1924) T247.

as shown in figures 5 and 6. One division on the scale of the milliammeter connected to the telemeter corresponded to a strain in the column of about 0.001 in. in the gage length of 8 in. The range of these instruments was 10 divisions, equivalent to a strain of 0.00125 (in./in.).

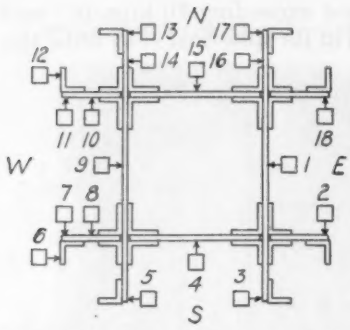

FIGURE 5.—*Location of the telemeters (indicated by squares) on a column.*

The telemeters were calibrated before the columns were tested and the strain in the columns computed from the calibration factor and the reading of the milliammeter.

(3) *Lateral Deflection.*—The diaphragms projecting from the test column precluded the use of the taut wire and mirror-scale deflectometer for measuring the lateral deflection. Therefore a frame of structural steel shown in figure 7 was erected around the lower half of each of the columns after it had been centered in the testing machine. The frame was bolted to the lower bearing plate. The upper end of the frame, at midheight of the column, was used as a base for measuring the deflection of the column under load. Dial micrometers attached to rods of suitable length were used manually to measure the distance between the frame and the column by inserting the conical ends of the spindle and of the rod into deflection points (center punch marks) in the frame and in the column. One division on the dial was 0.001 in. Two observers took the readings on opposite sides of the column simultaneously. For each load increment, readings were taken at the 44 stations shown in figure 8, 11 on each side of the column.

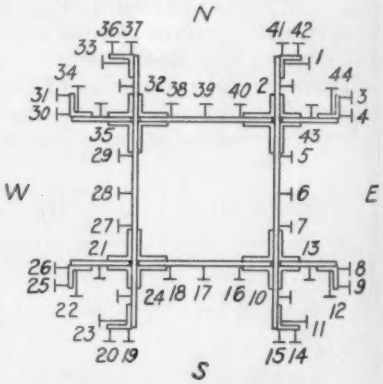

FIGURE 8.—*Stations (indicated by lines) at which lateral deflection was measured at midheight of a column.*

(4) *Loading.*—For 1 column of each of the three kinds of steel the load was increased by increments until the deflection of the column brought it into contact with the compressometers. The compressometers were then removed and the pump of the testing machine operated at a constant speed. Load readings were taken at intervals of 1 minute until the load had reached the maximum and then decreased. The load increments were equivalent to an average stress of 4 kips/in.^{2} in the column until the maximum load was approached; thereafter the increments were smaller. The compressometers, the telemeters, and the lateral deflections were read for each increment of load until the compressometers were removed.

The other columns were loaded in the same way, except that when the load approached the end of the elastic range of the column, the

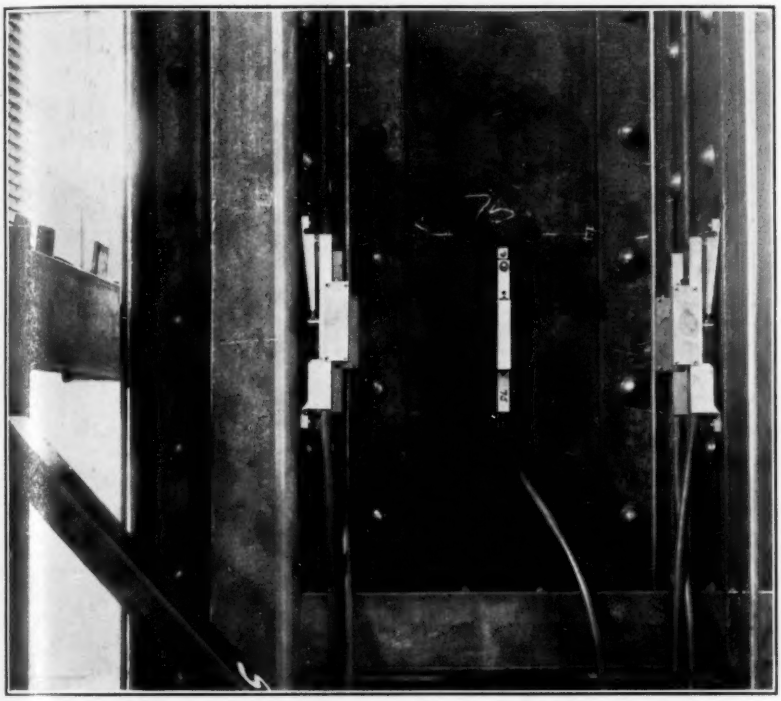

FIGURE 6.—*Telemeters (8-in. gage) near midheight on the north side of a column.*

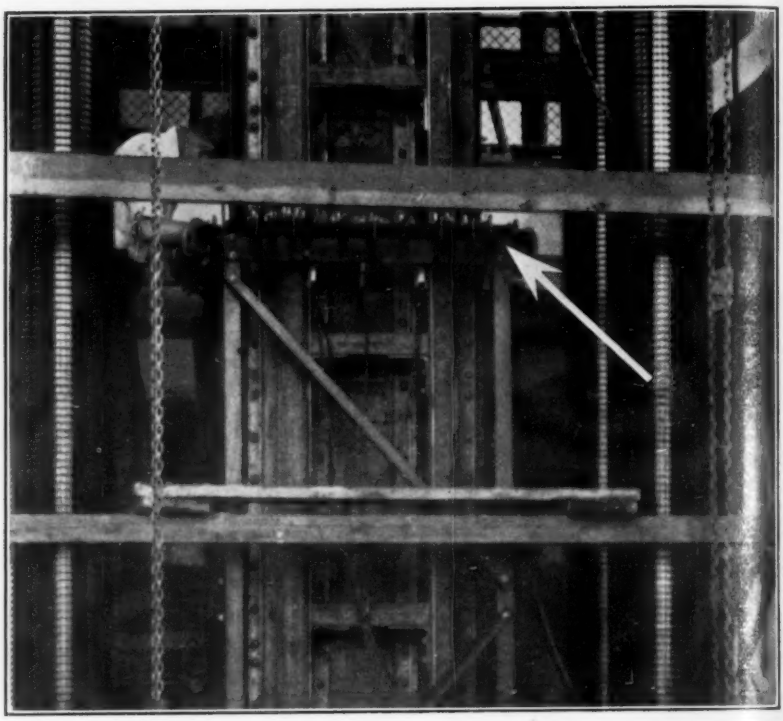

FIGURE 7.—*Frame used as a base for measuring the lateral deflections at midheight of a column.*

load was decreased to a low value once and then increased until the column had yielded plastically, when the load was again decreased to a low value once and then increased to the maximum.

5. METHOD OF DETERMINING THE PROPERTIES OF THE COLUMNS

(a) YOUNG'S MODULUS

The average Young's modulus of elasticity for each column was determined from the values of average stress and average compressometer strain. The average stress was obtained by dividing the load by the nominal cross-sectional area of the column. The arithmetical average of the 16 compressometer strains for each load was taken as the average compressometer strain. The computed strains obtained by dividing the average stresses in the elastic range by a trial modulus were compared with the average compressometer strains. The trial modulus for which the computed strains agreed most closely with the compressometer strains for loads within the elastic range was taken as the Young's modulus of elasticity of the column.

(b) PROPORTIONAL LIMIT

A proportional limit for each column was determined as the stress for which the average compressometer strain was 0.000012 greater than the strain computed by the use of the Young's modulus.

(c) COLUMN YIELD STRENGTH

For reasons discussed later, the yield strength of the column was taken as the stress for which the average compressometer strain was 0.002 greater than the strain computed by using the Young's modulus. The value for each column was obtained graphically from the stress-strain graph for the column.

(d) WEIGHTED YIELD STRENGTH OF THE MATERIAL

The weighted average tensile yield strength of the material in the column was obtained from the yield strengths of coupons by weighting them in the ratio of the cross-sectional area of the main member which they represented to the total nominal cross-sectional area of the column.

(e) COLUMN EFFICIENCY

The column efficiency was obtained by dividing the column yield strength by the weighted yield strength of the material in the column.

6. COUPONS

(a) GENERAL

The coupons were machined from the pieces marked "Coupon" in the cutting diagram in figure 1. This diagram shows the relation of the coupons to the longitudinal pieces used in fabricating each column. From each of the plates 34⅜ in. wide for the columns TC1, TS1, and TM1, two coupons were taken, one at the middle and one at the edge of the plate. For all the other plates one coupon was taken at the

middle of the plate. For all of the angles one coupon was taken at the middle of one of the legs of the angle.

(b) SHAPE AND SIZE

The axis of each coupon was parallel to the rolling direction (axis) of the plate or angle. The coupons were standard ASTM tensile specimens for plates, shapes, and flats.[6] These coupons had a gage length of 8 in., a width at the reduced section of 1½ in., and the thickness was that of the material as rolled.

(c) YIELD STRENGTH

The method selected for determining the yield strength of these coupons is essentially the "set method" described by the Section on Elastic Strength of Material of the Technical Committee on Mechanical Testing of the American Society for Testing Materials.[7] The yield strength was taken as the stress for which the strain was 0.002 greater than the strain computed from the stress and the Young's modulus of elasticity. The values obtained in this way agreed closely with those obtained by the drop of beam for those coupons which showed a definite drop of beam. For some of the carbon steel coupons no strain measurements were made and the yield strength was determined by the drop of beam method.

(d) TESTING MACHINE

The coupons were tested in a screw-power, beam-and-poise machine having a capacity of 100 kips.

(e) EXTENSOMETER

The strains in some coupons of each kind of steel were measured by the use of a Ewing extensometer having a gage length of 8 in. One division on the scale of this instrument corresponded to a strain of 0.000025 in the coupon. The readings were estimated to 0.1 division. For the coupons of silicon and of carbon-manganese steel upon which a Ewing extensometer was not used, the strains were measured by the use of a Berry strain gage having a gage length of 8 in. The yield strength was determined graphically by a method which gave values approximating closely those obtained by the use of the Ewing extensometer.

(f) SPEED OF THE MOVABLE PLATEN

For the coupons on which a Ewing extensometer was used, the speed of the movable platen of the testing machine under no load was 0.04 in./min and this speed was maintained until the stress was about three-quarters of the yield strength. For higher stresses the speed was 0.01 in./min. After the extensometer was removed the speed was 0.4 in./min until the coupon ruptured.

For the coupons on which a Ewing extensometer was not used, the speed was 0.04 in./min until the yield strength was observed. For higher stresses the speed was 0.4 in./min.

[6] Figure 1, Stand. Am. Soc. Testing Materials [I] **68** (1933).
[7] Proc. Am. Soc. Testing Materials [I] **31**, 602 (1931).

III. RESULTS FOR THE COUPONS

1. TENSILE TESTS

The results of the tensile tests of the coupons are given in table 3. The properties of the material are average values for the longitudinal members of the same size and shape. The values of the yield strength are drop-of-beam values for the carbon-steel coupons and stress-strain graph values for the silicon and the carbon-manganese-steel coupons.

TABLE 3.—*Results of the tensile tests of coupons*

Column material		Number of coupons tested	Yield strength (average)	Tensile strength (average)	Elongation in 8 in. (average)	Reduction of area (average)
Shape	Nominal size, in.					
			kips/in.²	kips/in.²	*Percent*	*Percent*
COLUMN TC1—CARBON STEEL						
2 plates	34⅜ by ⅝	4	32.7	57.4	31.4	56.7
2 plates	17 by ⅝	2	33.5	57.4	31.8	58.8
4 plates	7⅝ by ⅝	4	31.4	56.3	31.2	61.0
4 angles	4 by 4 by 9/16	4	33.0	57.5	31.6	55.8
8 angles	4 by 3 by ½	8	32.8	58.8	27.4	54.9
12 angles	3 by 3 by ½	12	39.2	63.3	28.4	53.1
Weighted average			34.0	58.7	30.2	56.4
COLUMN TC2—CARBON STEEL						
2 plates	34⅜ by ⅝	2	31.7	57.6	30.0	58.0
2 plates	17 by ⅝	2	33.1	56.6	32.6	60.8
4 plates	7⅝ by ⅝	4	31.5	56.2	32.9	58.8
4 angles	4 by 4 by 9/16	4	32.4	57.0	31.5	56.4
8 angles	4 by 3 by ½	8	33.9	59.4	28.3	55.8
12 angles	3 by 3 by ½	12	39.4	63.3	28.0	51.5
Weighted average			33.9	58.7	30.2	56.6
COLUMN TS1—SILICON STEEL						
2 plates	34⅜ by ⅝	4	55.1	96.8	17.6	41.5
2 plates	17 by ⅝	2	42.8	78.0	22.8	48.8
4 plates	7⅝ by ⅝	4	48.2	91.7	19.8	44.6
4 angles	4 by 4 by 9/16	3	51.1	88.5	21.1	44.8
8 angles	4 by 3 by ½	8	55.2	93.9	18.2	45.1
12 angles	3 by 3 by ½	12	58.3	94.3	19.8	45.8
Weighted average			52.9	91.8	19.5	44.7
COLUMN TS2—SILICON STEEL						
2 plates	34⅜ by ⅝	2	51.4	91.9	20.6	44.0
2 plates	17 by ⅝	2	43.8	78.6	20.5	47.8
4 plates	7⅝ by ⅝	4	48.5	91.3	19.4	42.3
4 angles	4 by 4 by 9/16	4	53.2	91.9	20.3	45.4
8 angles	4 by 3 by ½	8	55.6	94.1	18.7	43.8
12 angles	3 by 3 by ½	12	59.2	96.4	20.4	45.5
Weighted average			52.5	91.3	20.1	44.7
COLUMN TM1—CARBON-MANGANESE STEEL						
2 plates	34⅜ by 9/16	4	58.9	99.5	18.9	48.3
2 plates	17 by 9/16	2	54.9	94.8	20.9	48.0
4 plates	7¾ by 9/16	4	56.6	98.8	18.0	44.9
4 angles	4 by 4 by 9/16	4	55.7	93.4	22.0	51.8
8 angles	4 by 3 by ½	8	56.5	94.7	18.7	43.6
12 angles	3 by 3 by ½	12	56.0	93.4	20.1	51.0
Weighted average			56.7	96.0	19.6	48.9

TABLE 3.—*Results of the tensile tests of coupons*—Continued

COLUMN TM2—CARBON-MANGANESE STEEL

Column material		Number of coupons tested	Yield strength (average)	Tensile strength (average)	Elongation in 8 in. (average)	Reduction of area (average)
Shape	Nominal size, in.					
			kips/in.[2]	kips/in.[2]	*Percent*	*Percent*
2 plates	34⅜ by 9/16	2	59.8	102.1	19.2	48.8
2 plates	17 by 9/16	2	55.0	96.0	20.8	51.0
4 plates	7¾ by 9/16	4	56.2	97.6	18.5	49.1
4 angles	4 by 4 by 9/16	4	55.6	92.5	20.8	54.7
8 angles	4 by 3 by ½	8	56.7	94.7	19.0	49.7
12 angles	3 by 3 by ½	12	56.2	93.9	20.1	49.7
Weighted average			57.0	96.7	19.7	48.6

Ewing stress-strain graphs for typical coupons of the 3 kinds of steel are shown in figure 9.

The speed of the movable head was much lower than is customarily used when determining the yield strength. If the yield strength is

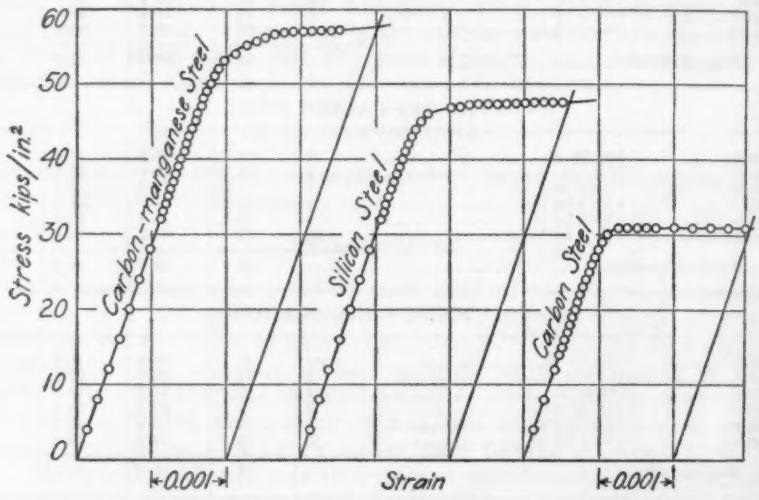

FIGURE 9.—*Typical Ewing stress-strain graphs for the 3 kinds of steel.*

determined by the drop of the beam the value is dependent on the speed—the higher the speed, the higher the yield strength.[8] For these coupons the rate at which the stress was increased is more nearly the rate for the columns than the rate customarily used for coupons.

2. CHEMICAL COMPOSITION

Chemical analyses were made by the Chemistry Division of samples from the coupons having the highest and the lowest tensile strength for each kind of steel, each thickness, and each shape. The results are given in table 4.

[8] Proc. Am. Soc. Testing Materials [I] 28, 105 (1928).

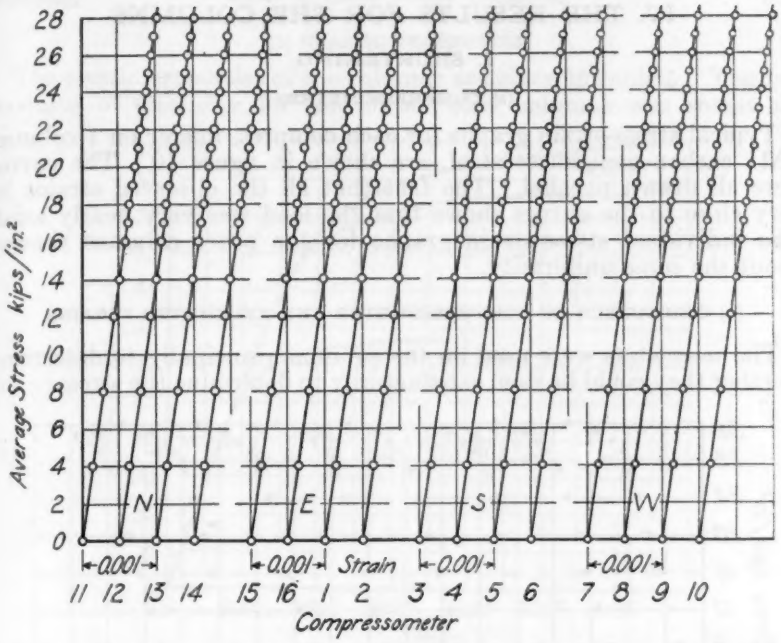

FIGURE 10.—*Typical stress-strain graphs for each compressometer on one column, TM1 carbon-manganese steel.*

The maximum stress was 61.6 kips/in.².

TABLE 4.—*Chemical composition of the steels*

CARBON STEEL

Description of samples			Chemical composition				
Thickness	Shape	Tensile strength	Carbon	Manganese	Phosphorus	Sulphur	Silicon
in.		kips/in.²	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*
½	Angle	55.1	0.18	0.56	0.015	0.033	0.03
½	do	66.9	.24	.55	.018	.037	.03
9/16	do	53.3	.14	.46	.012	.031	.02
9/16	do	61.0	.18	.53	.026	.048	.04
5/8	Plate	53.0	.14	.33	.009	.023	.11
5/8	do	61.6	.19	.46	.019	.022	.11

SILICON STEEL

½	Angle	84.9	0.34	0.80	0.030	0.038	0.25
½	do	109.0	.43	1.09	.029	.039	.35
9/16	do	84.1	.44	.81	.018	.029	.29
9/16	do	102.8	.41	1.07	.036	.032	.34
5/8	Plate	75.5	.31	.63	.009	.023	.29
5/8	do	98.8	.44	.80	.029	.027	.34

CARBON-MANGANESE STEEL

½	Angle	89.8	0.30	1.47	0.027	0.019	0.18
½	do	99.7	.37	1.54	.030	.022	.17
9/16	do	90.7	.30	1.54	.028	.018	.17
9/16	do	95.6	.33	1.50	.027	.020	.18
9/16	Plate	93.6	.30	1.67	.028	.022	.18
9/16	do	105.2	.36	1.72	.023	.026	.17

IV. THE RESULTS FOR THE COLUMNS

1. SHORTENING

(a) COMPRESSOMETERS

Typical stress-strain graphs for each compressometer on 1 column, TM1 carbon-manganese steel, are shown in figure 10. The curves were all drawn parallel. The fact that all the observed strains lie very close to the curves shows that the load was very nearly axial. The individual stress-strain graphs for the other columns showed about the same uniformity.

(b) COMPARISON OF COMPRESSOMETER AND TELEMETER STRAINS

The telemeters were used on the columns principally to determine whether they could be used satisfactorily to determine the stress in the

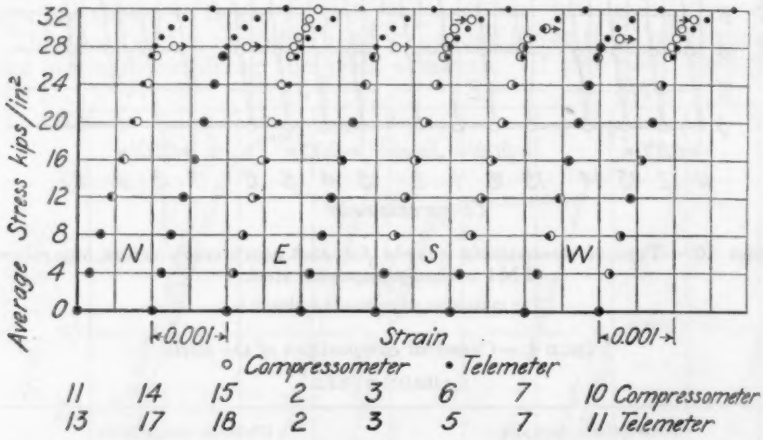

FIGURE 11.—*Stress-strain graphs for the compressometers and for the telemeters which were on the same main members of column* TC1 *carbon steel.*

The maximum stress was 36.9 kips/in.².

steel. On the columns eight of the telemeters were on main members of the column having compressometers. The typical stress-strain graphs shown in figure 11, on one column (TC1 carbon steel) for the last loading, indicate that the compressometers and telemeters gave nearly the same values within the elastic range and that the stress at midheight of the column was nearly the same as the average stress computed from the compressometer readings.

(c) AVERAGE STRESS-STRAIN GRAPHS

The average value of the strains indicated by the 16 compressometers for each load is plotted against the stress for columns TC2, TS1, and TM1 in figure 12. On these columns the load was increased continuously until failure occurred. The corresponding graphs for columns TC1, TS2, and TM2, for which the load was released before failure occurred, are shown in figure 13 together with the graphs of figure 12. These graphs may be compared with the tensile stress-strain graphs for typical coupons shown in figure 9.

(d) ELASTIC PROPERTIES

The elastic properties of the columns are given in table 5. Young's modulus of elasticity for the carbon-steel columns was somewhat

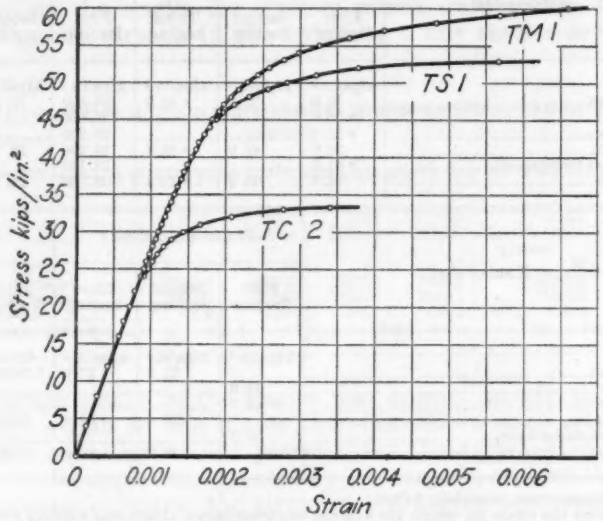

FIGURE 12.—*Stress-strain graphs for the columns on which the load was not released.*
The average compressometer strains were plotted.

higher than for the other columns. For the carbon-steel and silicon-steel columns on which the load was released, the modulus was slightly

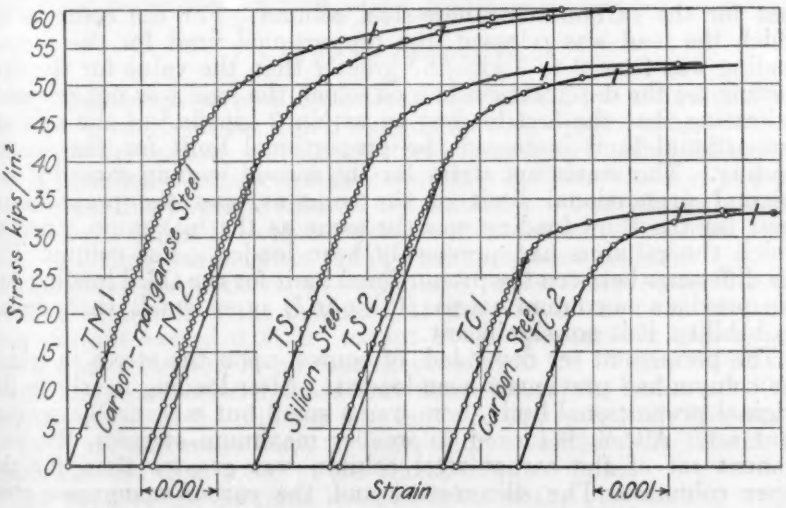

FIGURE 13.—*Stress-strain graphs for the columns.*
The average compressometer strains were plotted. The average of the maximum stresses for the carbon-manganese-steel columns was 62.0 kips/in.²; for the silicon-steel columns, 55.2 kips/in.²; and for the carbon-steel columns 36.8 kips/in.².

greater for the second and third loading than for the first loading. For the carbon-manganese-steel columns the modulus was the same for each of the three loadings.

TABLE 5.—*Elastic properties of the columns*

Column number	Kind of steel	Maximum stress for—			Young's modulus of elasticity		
		First loading	Second loading	Third loading	First loading	Second loading	Third loading
		kips/in.²	kips/in.²	kips/in.²	kips/in.²	kips/in.²	kips/in.²
TC1	Carbon	19.0	27.0	• 36.9	28,500	28,700	28,700
TC2	do	• 36.8			29,100		
TS1	Silicon	• 55.7			28,200		
TS2	do	24.0	40.0	• 54.8	28,200	28,500	28,500
TM1	Carbon-manganese	• 61.6			28,150		
TM2	do	24.0	40.0	• 62.3	28,350	28,350	28,350

Column number	Kind of steel	Proportional limit [b]			Set after	
		First loading	Second loading	Third loading	First loading	Second loading
		kips/in.²	kips/in.²	kips/in.²	*Strain*	*Strain*
TC1	Carbon	[c]	21.0	27.0	0.000027	0.000169
TC2	do	19.0				
TS1	Silicon	25.0				
TS2	do	[c]	28.0	39.0	.000021	.000145
TM1	Carbon-manganese	26.0				
TM2	do	[c]	28.0	40.0	.000013	.000143

• Final maximum stress, preceding failure.
[b] Determined as the stress for which the average compressometer strain was 0.000012 greater than the strain computed by the use of the Young's modulus of elasticity.
[c] Not reached.

For the columns on which the load was not released the values given for the first loading may be taken as the original proportional limit. The value for the silicon-steel column is almost the same as that for the carbon-manganese-steel column. For the columns on which the load was released, the proportional limit for the second loading was from 2 to 3 kips/in.² greater than the value for the first loading for the duplicate column on which the load was not released, indicating that the first loading to within 2 kips/in.² of the original proportional limit increased the proportional limit for the second loading. The maximum stress for the second loading exceeded the original proportional limit of the columns, and the proportional limit for the third loading was the same as the maximum stress to which the columns had previously been loaded. For column TS2 the difference between the proportional limit for the third loading and the previous maximum stress (1 kip/in.²) is so small that, in all probability, it is not significant.

The permanent set depended, of course, upon the stress to which the column had previously been loaded. After loading nearly to the original proportional limit there was a small but measurable permanent set. Although loaded to smaller maximum stresses, the permanent set of the carbon-steel column was greater than for the other columns. The silicon-steel and the carbon-manganese-steel columns were loaded to the same maximum stresses, but the permanent sets were less for the carbon-manganese-steel column.

(c) COMPARISON OF STRAINS IN PLATES AND ANGLES

The stress-strain graphs, figure 10, for the compressometers on the plates and on the angles show that for stresses within the elastic ranges of the columns there was no appreciable difference between

the strains in the plates and in the angles and therefore that the stresses were practically the same.

The average strain was computed for compressometers 2, 3, 6, 7, 10, 11, 14, and 15 on the plates and for compressometers 1, 4, 5, 8, 9, 12, 13, and 16 on the angles for stresses which were within 4 kips/in.^{2} of the maximum stresses in the columns. The results are given in table 6.

TABLE 6.—*Comparison of the compressometer strains in plates and in angles of the columns*

[The plus sign indicates that the strain in the angles was greater than the strain in the plates]

Column no.	TC1	TC2	TS1	TS2	TM1	TM2
Steel	Carbon	Carbon	Silicon	Silicon	Carbon-manganese.	Carbon-manganese.
Average stress, kips/in.^{2}	33	33	52	52	60	60
Average strain in plates	.002495	.002756	.003789	.004015	.006582	.006278
Average strain in angles	.002527	.002800	.003793	.004011	.006617	.006297
Difference, percent	+1.3	+1.6	+0.1	−0.1	+0.5	+0.3
Average difference, percent	+1.4		0.0		+0.4	

The average strain in the angles was approximately the same as the average strain in the plates; for the silicon-steel columns, the strains were equal within 0.1 percent; for the carbon-steel columns, the strain in the angles was greater by 1.4 percent, and for the carbon-manganese-steel columns, the strain in the angles was greater by 0.4 percent.

The difference in the average stress in the angles and in the plates was much less than the difference in the strains because near the maximum stress the stress-strain curve is almost parallel to the axis of strain. The longitudinal members of the steel tower columns, therefore, behaved as a unit under compressive loads.

2. LATERAL DEFLECTION

The deflections at each deflection point are shown in figure 14 for a stress on each column which was within 4 kips/in.^{2} of the maximum stress for the carbon- and silicon-steel columns and within 7 kips/in.^{2} for the carbon-manganese-steel columns. For convenience, the deflections of the opposite sides of the column are both plotted on the side toward which the column deflected, dotted and solid lines being used to distinguish between the deflections of the two sides.

The difference between the solid and dotted lines represents the local deformation of the section. At these loads the local deformation did not exceed 0.05 in., except at the outstanding angles, and the lateral deflection in no case exceeded 0.25 in. These values are small in comparison with the lateral dimensions of the sections (34½ in.) and the length of the columns (288 in.). At approximately 90 percent of the final maximum load, the maximum observed deflection in all cases was less than 0.001 of the length of the column.

For most of the columns the deflection of the outstanding angles (a3, fig. 1) was about the same as that of the plates, showing that at these high loads there was no change of any importance in the relative positions of the main members under load. The columns behaved as sturdy columns, no significant weakening by local deformation occurring until marked plastic deformation had been produced in the column as a whole.

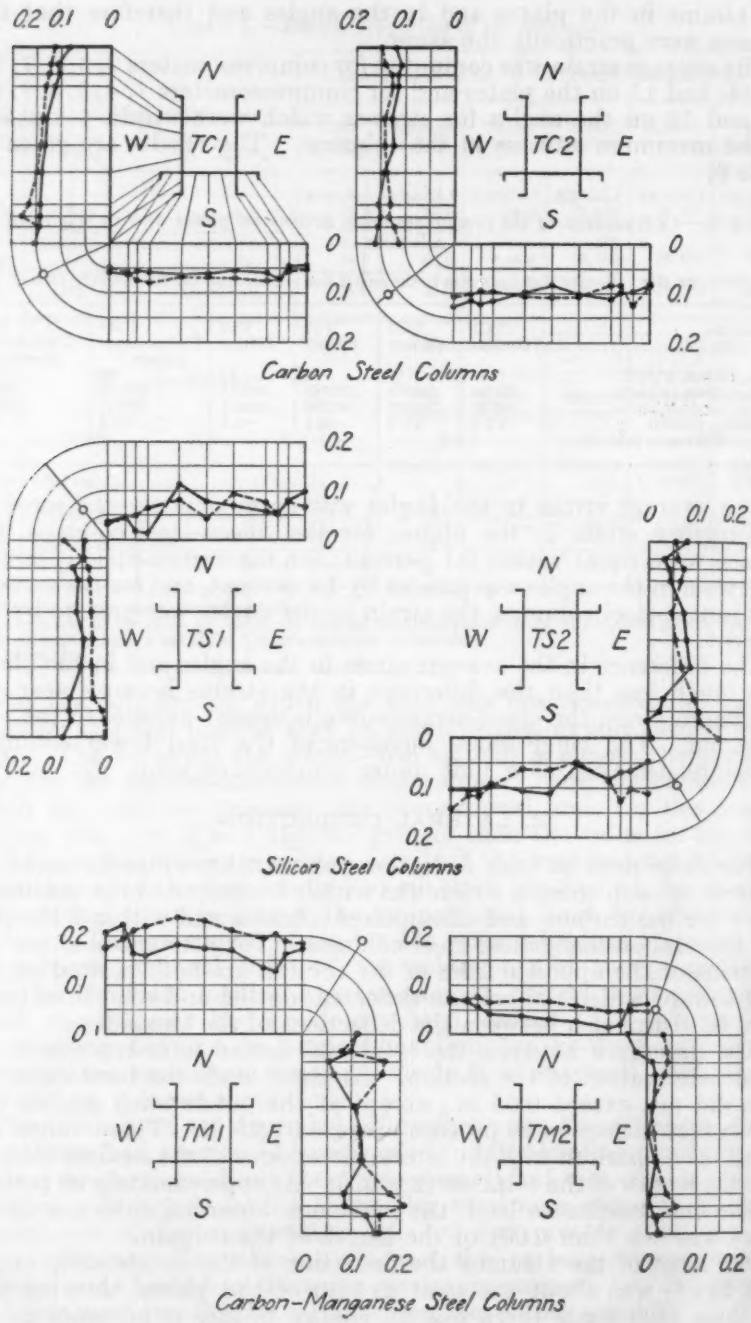

FIGURE 14.—*The lateral deflection at each station for stresses of 33.0* kips/in.² *in the carbon-steel columns, 52.0* kips/in.² *in the silicon-steel columns, and of 57.0* kips/in.² *in the carbon-manganese-steel column* TM1 *and of 55.0* kips/in.² *in column* TM2.

The average values of the deflections for each side of the columns are shown in figure 15. For columns TC1, TS2, and TM2, upon which the load was released, the values for the last loading were used. In general, the deflection increased for increased stresses and at a rapidly increasing rate as the final maximum stress for the columns was approached.

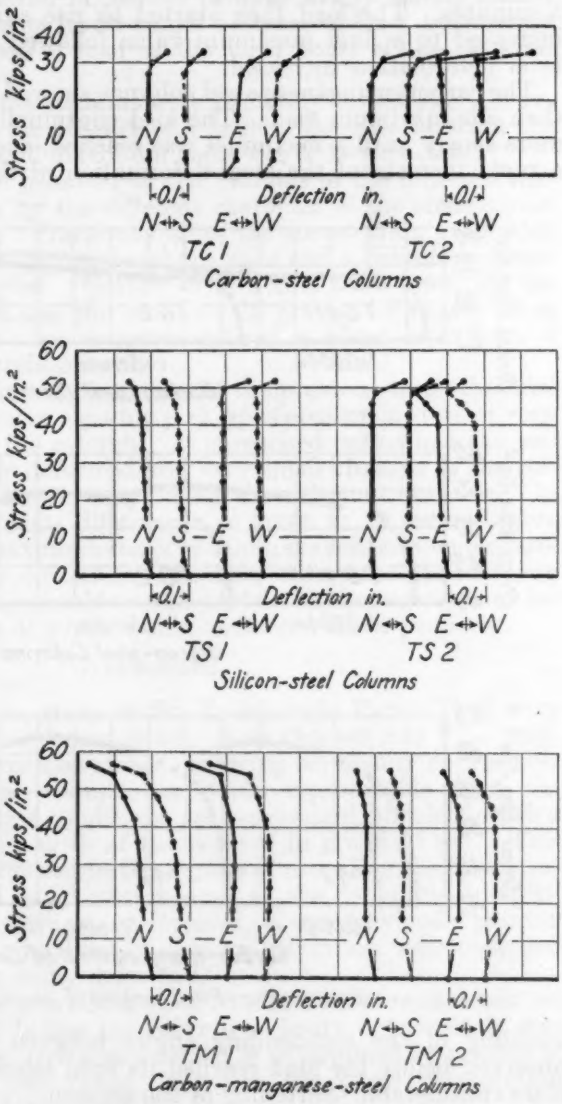

FIGURE 15.—*Average values of the deflections for each side of the columns at different loads.*

3. MAXIMUM LOAD

(a) FINAL LOADING

As the maximum load was approached the readings were taken for each increase in stress of 1 kip/in.^{2} until the column began to deform plastically, as indicated by the continuous operation of the pump of the testing machine to keep the beam balanced at a given, or slowly increasing, load and also by the continuous, slow increases in the readings of the compressometers. The compressometers and the frame for measuring deflections were then removed, and the pump was operated continuously at a speed which caused a shortening of the column of about 0.1 in./min. The load was recorded each minute until it reached its final maximum value and then decreased. The results are shown in figure 16.

The carbon-steel columns showed definite "first maximum" loads, the loads holding nearly constant for some 20 minutes of continuous pumping, and in the case of column TC2 showing a slight but definite decrease. On further pumping, the loads on these columns picked up

to second maximum values and then decreased with rapidly increasing local deformation.

The silicon-steel columns showed no definite first maximum load, but with continuous pumping the load increased very slowly for over 5 minutes. The load then started to rise again more rapidly and increased to a final maximum value followed by a decrease as the local deformation increased.

The carbon-manganese-steel columns showed no indication of more than one maximum load. The load continually increased more and more slowly until a maximum was reached, and then decreased with a rapid increase of the local deformation of the column. Incipient

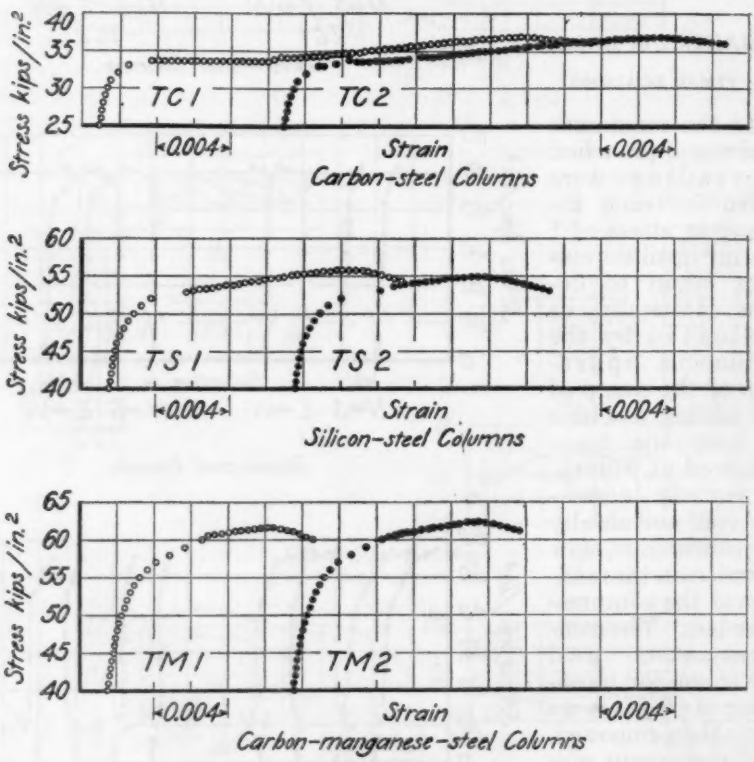

FIGURE 16.—*Final loading of the columns.*

buckling of the outstanding angles between the diaphragms was observed before the load reached its final maximum value, but only after considerable shortening of the column.

(b) "PICK-UP" OF LOAD

The behavior of these columns is similar in this respect to that of some of the small specimens tested by von Kármán.[9]

The behavior of the carbon-steel columns in particular is also similar to that of the heavy 12-foot H columns (l/r=37.8 to 40.5) tested some years ago at the Bureau.[10] In those tests, after the first maxi-

[9] Th. von Kármán. Untersuchungen über Knickfestigkeit, Mitt. über Forsch. arb. (VDI) **81**, 31 (1910).
[10] BS Tech. Pap. **21**, (1926) T328. See particularly p. 57–60.

mum load was passed the stress fell off by amounts ranging from about 0.2 kip/in.^{2} to over 2.0 kips/in^2. before the increase to the second maximum load began. In discussing these tests it was pointed out that [11] "for still shorter or heavier or more nearly axially loaded columns, there might even be no actual decrease of load, but merely a slower rate of increase of load as the yield point of the material was passed."

In the present tests the columns were relatively considerably heavier (l/r=28.9) so that the absence of a definite decrease between the first maximum and second maximum loads was to be expected.

The difference in the behavior of the columns of the different materials is accounted for by the different character of the stress-strain graph for the material. Practically all of the stress-strain graphs for the carbon-steel coupons showed a sharp knee and a definite horizontal portion, or yield point. Graphs of this kind were fewer for the coupons of silicon steel and the stress-strain graphs for nearly all of the carbon-manganese-steel coupons showed a blunt knee with a continual rise as the strain increased.

As was pointed out in the discussion of the previous tests, the final maximum load of a column showing pick-up represents a state of very precarious stability of the column. It is reached only when the columns are already badly deformed and very small changes in the columns or the test conditions may make the columns unstable. In the previous series of tests differences as great as 15 percent were observed in the final maximum loads of duplicate columns under carefully controlled test conditions. The final maximum load of any column showing pick-up should not be used for designing columns for a structure, the failure of which would endanger life or property.

(c) STRENGTH

The column strengths given in BS Technologic Paper T328 were the values of the first maximum stress. It was stated that "the practically definite first maximum stress, occurring before any appreciable lateral deflection of the column, and fairly reproducible when the column material and test conditions are reproduced, should furnish a good measure of the strength of the column in practical use. This justifies the practice followed in this report of recording the first maximum stress observed in a column test as the 'column strength' under the given test conditions. However, as was previously pointed out, this would not be justified in case no maximum were observed before the column was badly deformed."

With regard to the procedure that should be followed when no maximum is observed before the column is badly deformed, it was stated that "the best criterion could only be determined by a series of tests on columns in this range, in which the stress deformation curves were carefully determined."

In tensile tests of steels which do not show a definite yield point, it has become customary to define a yield strength in terms of the stress necessary to produce a definite strain (usually 0.002) in the coupon in excess of the computed elastic strain. It seemed probable that a similar definition of a column yield strength would be satisfactory for columns for which no definite first maximum load is observed, and for this reason the column yield strengths were computed on this basis.

[11] BS Tech. Pap. **21**, 59 (1926) T328.

The column yield strength, the first maximum and final maximum stress, and the column efficiency are given in table 7. For the carbon-steel and silicon-steel columns for which a definite first maximum load was observed, the column yield strength is substantially identical with the first maximum stress. An examination of the data in BS Technologic Paper T328 shows that a similar relation holds for the shorter columns which showed hang-on or pick-up of load.

TABLE 7.—*Strength and efficiency of the columns*

Column number	Kind of steel	Final maximum load	Weighted yield strength of material	Column yield strength[1]	First maximum stress	Final maximum stress	Column efficiency (based on column yield strength)
		kips	kips/in.^{2}	kips/in.^{2}	kips/in.^{2}	kips/in.^{2}	*Percent*
TC1	Carbon	5,860	34.0	33.4	33.6	36.9	98
TC2	do	5,846	33.9	33.3	33.5	36.8	98
	Average	5,853	34.0	33.3	33.5	36.8	98
TS1	Silicon	8,862	52.9	51.9	53.0	55.7	98
TS2	do	8,720	52.5	51.6	53.5	54.8	98
	Average	8,791	52.7	51.7	53.2	55.2	98
TM1	Carbon-manganese	9,293	56.7	56.8	----------	61.6	100
TM2	do	9,402	57.0	57.2	----------	62.3	100
	Average	9,348	56.8	57.0	----------	62.0	100

[1] Stress for which the strain is 0.002 greater than the elastic strain.

The column yield strength for the silicon-steel columns was 1.55 times that for the carbon-steel columns. For the carbon-manganese-steel columns it was 1.71 times that for the carbon-steel columns.

The column efficiency was 98 percent for the carbon-steel and for the silicon-steel columns and 100 percent for the carbon-manganese-steel columns.

Since the speed of the movable platen of the testing machine used for determining the yield strength of the coupons (0.01 to 0.04 in./min) was lower than that customarily used (up to 2 in./min on an 8-in. gage length), the yield strengths of the coupons were somewhat lower than those ordinarily obtained for structural steel. Had the customary speed been used, the values for the column efficiency would have been less.

The results in BS Technologic Paper T328 were corrected to a speed of 0.37 in./min on the basis of measurements at speeds of 0.012 and 0.37 in./min. The yield point observed at the higher speed was on the average 1.127 times that observed at the lower speed. Had the results been corrected to the lower speed instead of the higher, the efficiencies obtained for the columns having a slenderness ratio of about 40 would have ranged from 91 to 110 percent instead of 81 to 97 percent. Hence the efficiencies obtained in the present series of tests are consistent with those obtained in the previous tests when based on weighted yield strengths of the material obtained at the same speed.

The consistency of all these results indicates that in the case of sturdy columns which show no maximum load before the columns

FIGURE 17.—*A carbon-steel column,* TC2 *after test.*

The maximum stress was 36.0 kips/in². The deflection of the column from the cord at the left is apparent.

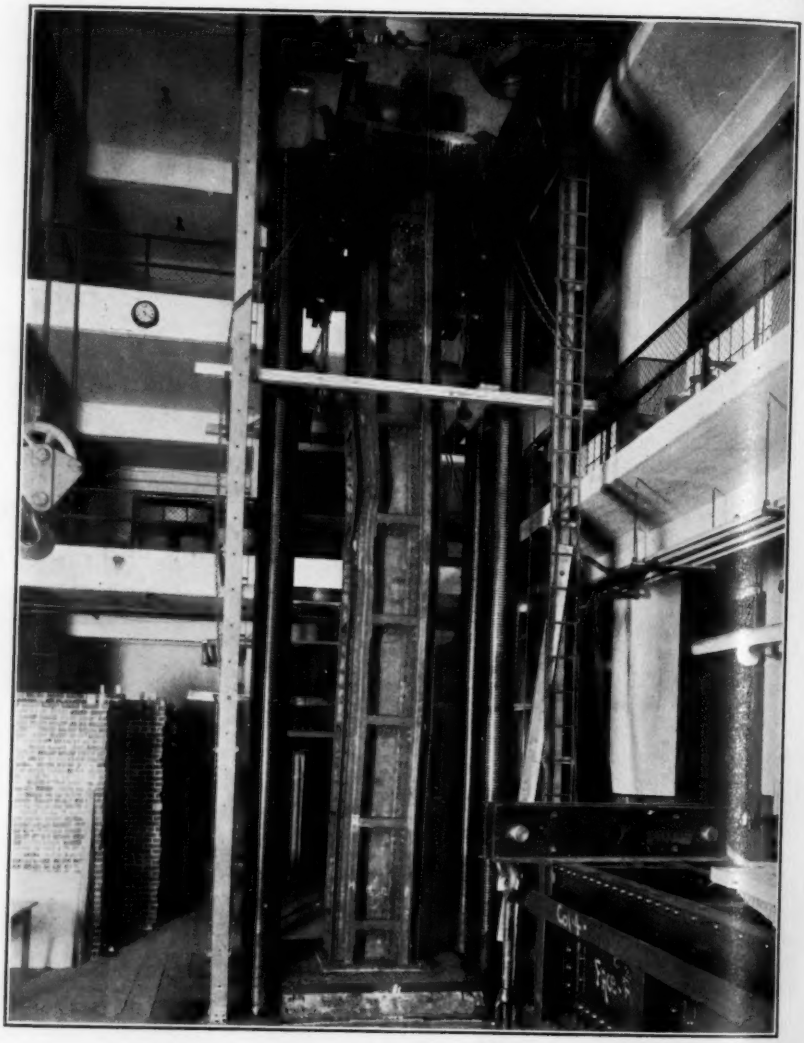

FIGURE 18.—*A silicon-steel column,* TS1, *after test.*

The maximum stress was 55.7 kips/in².

are markedly deformed, the column yield strength as here defined is a satisfactory practical measure of the strength of the column.

Further tests may indicate the possibility of defining a somewhat better measure, but the difference will be of little if any practical significance in large columns with their necessarily inhomogeneous material.

(d) DESCRIPTION OF THE FAILURE

For the carbon-steel (TC) and the silicon-steel (TS) columns the yield strength of the outstanding angles was greater than the weighted yield strength of the column material. For the carbon-manganese-steel (TM) columns the yield strength of the outstanding angles was somewhat less than the weighted yield strength of the column material. As the load was increased, Lüder's lines appeared on the plates of the carbon-steel and the silicon-steel columns before they appeared on the outstanding angles. As the load continued to increase, the deflection of the column as a whole caused buckling of the outstanding angles as shown in figures 17 and 18.

As the load was increased, Lüder's lines appeared on the outstanding angles of the carbon-manganese-steel columns before they appeared on the plates, as shown in figure 19. The way in which the carbon-manganese-steel columns failed is shown in figure 20.

For all the columns the outstanding angles buckled between the diaphragms on the concave sides of the column. Some shallow buckles also occurred in the plates and in the angles at the intersection of the plates. No rivets failed. The local buckling occurred only after considerable shortening of the column and was not the primary cause of failure. The primary failure was by plastic yielding as is also shown by the close agreement of the tensile yield strength of the material with the column yield strength when both are determined at comparable speeds of the testing machine.

V. CONCLUSIONS

1. The loading was nearly axial.

2. The strains under loads up to the end of the elastic range of the columns indicated by the compressometers and by the telemeters were very nearly the same.

3. The stress-strain graphs for the columns were very similar to those for the coupons.

4. Young's modulus of elasticity for the columns made from carbon steel was somewhat higher than that for the columns made from carbon-manganese steel and from silicon steel.

For the carbon-steel and the silicon-steel columns on which the load was released and then reapplied, the modulus was slightly greater for the second and third loading than for the first loading. For the carbon-manganese-steel columns, the modulus was the same for each of the three loadings.

5. The proportional limit was taken as the stress at which the observed strain exceeded the value computed from Young's modulus of elasticity by 0.000012. For the columns on which the load was not released the proportional limit was almost the same for the silicon-steel columns and for the carbon-manganese-steel columns. For the columns on which the load was released the proportional

limit for the second loading was from 2 to 3 kips/in.^{2} greater than for the first loading.

6. After loading to nearly the proportional limit for the first loading, there was a small but measurable set. The set was the least for the carbon-manganese steel and the greatest for the carbon-steel columns.

7. For stresses within the elastic ranges of the columns there was no appreciable difference between the strains in the plates and in the angles, and therefore the stresses were practically the same. For stresses beyond the elastic range of the columns, the average strain in the angles of the carbon-steel columns was 1.4 percent greater than the average strain in the plates; for the silicon-steel columns the strains were the same, and for the carbon-manganese-steel columns the strain in the angles was 0.4 percent greater. The differences in stress were much less than these values; therefore the plates and angles behaved as a unit under compressive loads.

8. For stresses which were nearly the maximum stresses in the columns the lateral deflections were very small. The deflections of the outstanding angles were about the same as those of the plates, showing that there was no significant change in the relative positions of the longitudinal members under load. Under load these columns behaved as sturdy columns.

9. The carbon-steel columns exhibited the phenomenon of pick-up, i. e., a definite first maximum load, a constant or slightly decreasing load for a considerable further shortening of the column, followed by a pick-up to a second higher maximum load after the columns were markedly deformed. The silicon-steel columns showed no definite first maximum load, but the load increased very slowly for a considerable shortening of the column and then more rapidly with further shortening. The carbon-manganese-steel columns showed no indication of more than one maximum load.

10. The column yield strength, taken as the stress for which the average strain is 0.002 greater than the elastic strain, appears to be a satisfactory measure of the strength of columns which do not show a maximum load before the column is deformed by that amount. The column yield strength for the silicon-steel columns was 1.55 times that for the carbon-steel columns. For the carbon-manganese-steel columns it was 1.71 times that for the carbon-steel columns. These ratios are practically the same as the ratios of the average yield strengths of the materials.

11. The practical constancy of these ratios is shown by the column efficiencies. For these columns having a slenderness ratio of 28.9, the column efficiency, defined as the quotient of the column yield strength divided by the weighted yield strength of the column material, was approximately 100 percent. For the carbon-manganese-steel columns the efficiency was 100 percent; for the carbon-steel and silicon-steel columns, 98 percent. These values are about the same as those observed in previous tests on columns having a slenderness ratio of about 40, when allowance is made for the effect of the speed of the testing machine on the yield strength of the column material.

12. For all the columns the outstanding angles buckled between the diaphragms on the concave sides of the columns. Shallow buckles also occurred in the plates and in the angles at intersection of the plates. No rivets failed. The local buckling occurred only after

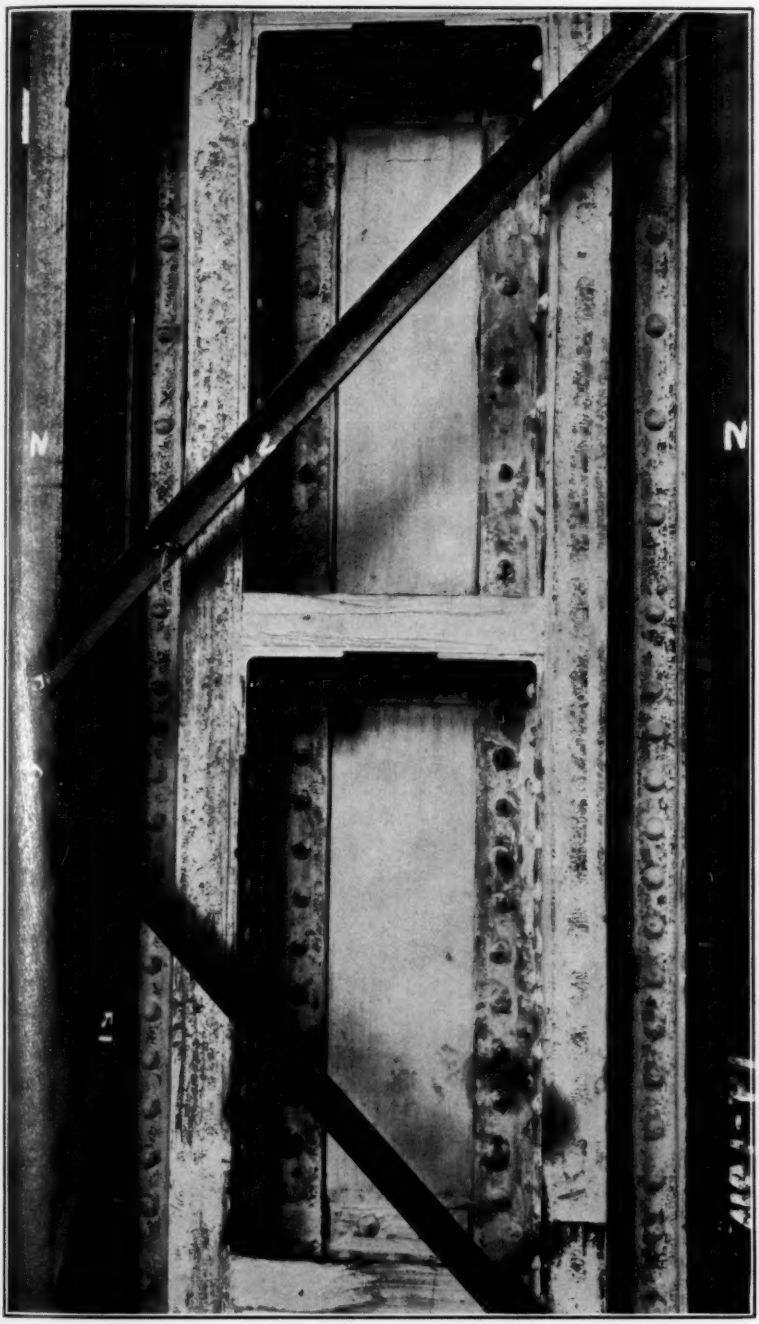

FIGURE 19.—*Lüder lines on the outstanding angles of a carbon-maganese-steel column* TM2.

No Lüder lines were observed on the plates.

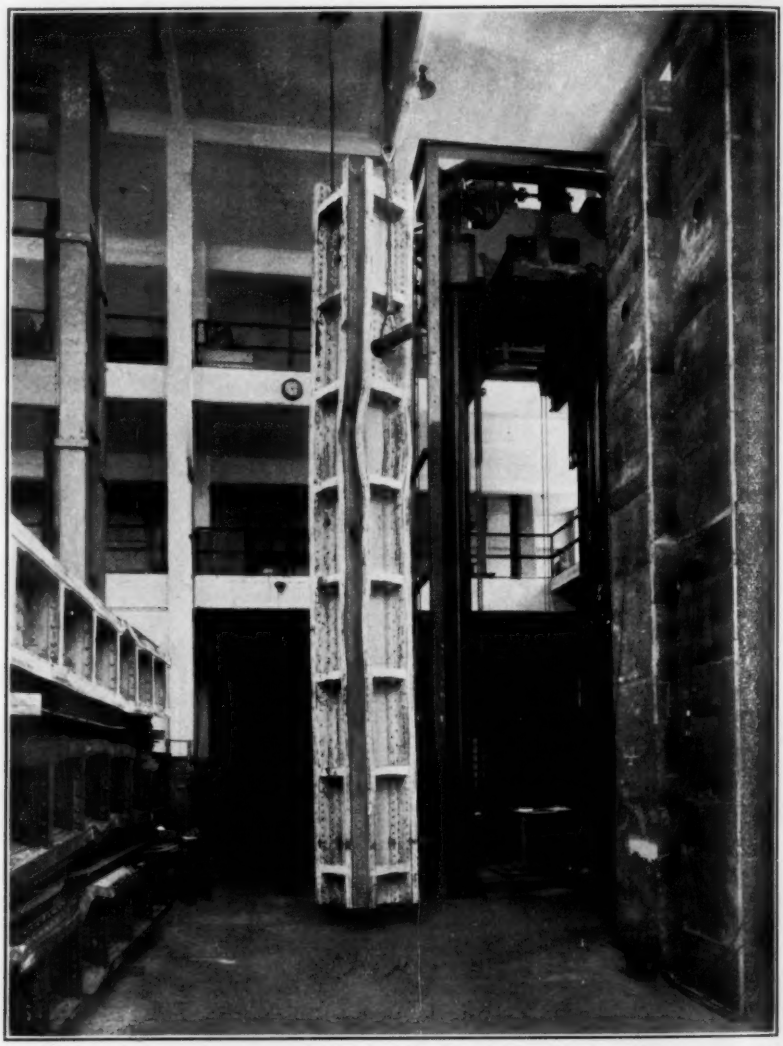

FIGURE 20.—*A carbon-manganese-steel column,* TM2, *after test.*
The maximum stress was 62.3 kips/in².

considerable shortening of the column and was not the primary cause of failure.

13. The tests confirm for these columns the conclusion from previous column tests that the tensile yield strength of the material determined at a speed of the testing machine comparable with that used in the column tests will furnish a close measure of the strength of short sturdy columns.

The program and testing procedure were prepared by O. H. Ammann, L. S. Moiseiff, and R. S. Johnston, representing the Port of New York Authority, and by L. J. Briggs, L. B. Tuckerman, and H. L. Whittemore, representing the National Bureau of Standards. The following members of the staff of the Port of New York Authority assisted in making the tests and obtaining the data: A. H. Baker, F. J. Hinners, S. K. Hoppen, B. H. Lefeve, L. D. Mork, R. B. Morris, and G. A. Woods.

WASHINGTON, July 29, 1935.

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